CHARLES GIBSON SITE #932063

Olin CHEMICALS
120 LONG RIDGE ROAD, P.O. BOX 1355, STAMFORD CT 06904-1355

VIA FEDERAL EXPRESS

March 12, 1985

Albert M. Bronson, Esq.
State of New York
Department of Law
State Office Building
65 Court Street
Buffalo, New York 14202

Gordon J. Johnson, Esq.
State of New York
Department of Law
Environmental Protection Bureau
Two World Trade Center
47th Floor, Room 4772
New York, New York 10047

Re: Pine & Tuscarora, Niagara Falls, New York

Dear Albert and Gordon:

Enclosed herein is the final draft of the Consent Judgment for the above-referenced matter for your final review.

Please call Rick Kennedy or me if you have any questions.

Very truly yours,

George H Pain

George H. Pain
Counsel

GHP:mvc

IN THE UNITED STATES DISTRICT COURT
FOR THE WESTERN DISTRICT OF NEW YORK

THE STATE OF NEW YORK, Plaintiff, v. OLIN CORPORATION, ARTHUR BATROUNY, BEVERLY JANE BATROUNY, JOHN ZITO, and ELIZABETH ZITO, Defendants.	Civil Action No. 83-1400

STIPULATION AND CONSENT JUDGMENT
APPROVING SETTLEMENT AGREEMENT

IN THE UNITED STATES DISTRICT COURT
FOR THE WESTERN DISTRICT OF NEW YORK

THE STATE OF NEW YORK, Plaintiff, v. OLIN CORPORATION, ARTHUR BATROUNY, BEVERLY JANE BATROUNY, JOHN ZITO, and ELIZABETH ZITO, Defendants.	Civil Action No. 83-1400

STIPULATION AND CONSENT JUDGMENT
APPROVING SETTLEMENT AGREEMENT

The undersigned, having agreed and stipulated that a consent judgment can be entered in this action incorporating a settlement agreement containing the following terms and conditions, and the Court having reviewed such terms and conditions, and having determined that they are reasonable and adequate to resolve the issues raised in this action, and constitute appropriate programs, using requisite remedial technology, to effectively protect the public health and environment consistent with the goals of the field investigations and remedial programs, and the Court being fully advised in the premises and having subject matter jurisdiction herein pursuant to 28 U.S.C.§1331, and 28 U.S.C. §1345,

NOW, THEREFORE, IT IS ORDERED AND ADJUDGED AS FOLLOWS:

INTRODUCTION

1. (a) The parties to this Agreement are:

(i) THE STATE OF NEW YORK, on behalf of the People of New York (hereinafter the "State");

(ii) OLIN CORPORATION, a corporation organized and existing under the laws of the State of Virginia (hereinafter "Olin");

(iii) JOHN and ELIZABETH ZITO, both residents of Niagara County, New York (hereinafter "Zito"); and

(iv) ARTHUR and BEVERLY JANE BATROUNY, both residents of Niagara County, New York (hereinafter "Batrouny").

(b) This Agreement pertains to the matter entitled The State of New York v. Olin Corp., Arthur Batrouny, et al., Civil Action No. CIV 83-1400 (hereinafter the a "Action") filed in the United States District Court, Western District of New York (hereinafter the "Court").

2. The Gibson site (hereinafter the "Site"), shown in Attachment 1, consists of two contiguous parcels of land owned respectively by Zito and Batrouny, including all rights of way within the boundaries of said two parcels. These two parcels consist of approximately four acres of land in Niagara County, bordered on the south by Pine Avenue, on the west by Tuscarora Road, and on the north and east by Cayuga Creek.

3. (a) In order to fulfill the purposes of this Agreement, Zito

and Batrouny shall cooperate fully with the State and Olin in allowing access to the Site and all structures and facilities erected thereon, as necessary, and in allowing and permitting the use and/or installation of appropriate sampling and testing devices, and excavations and borings on the Site, and in allowing necessary remedial actions, appropriate and necessary to fulfill the field investigations and remedial programs hereinafter described. Zito and Batrouny each shall execute and deliver to Olin, on a timely basis, such easements, rights of way, rights of entry, or other authorizations and approvals necessary to carry out any of Olin's obligations pursuant to this Agreement.

(b) Olin and the State will give Zito and Batrouny reasonable notice of all significant investigation and remedial activities to be conducted on the Site.

(c) Olin and the State will, to the maximum extent practicable, minimize interference with Zito's and Batrouny's use and enjoyment of the Site caused by actions called for by this Agreement and associated plans.

4. (a) The field investigations and remedial programs described in this Agreement have been or shall be designed to provide for, and shall have as goals, (i) the generation and analysis of data necessary to determine adequately the extent of chemical contamination of the Site and its environs which may have resulted from materials deposited or caused to be deposited on-Site by Olin or which may have migrated from the Site

following their deposit by Olin; and (ii) the design and implementation, in accordance with the schedule set forth herein, of remedial plans, based on the information generated through the field investigations, which to the extent achievable through the use of "requisite remedial technology" (as that phrase is defined below) will result in the removal from the Site and its environs or the isolation from people and the environment of contaminants which were deposited or caused to be deposited on-Site by Olin or of such contaminants which have migrated from the Site so as to effectively protect the public health and environment.

(b) Olin shall utilize requisite remedial technology to achieve the purposes set forth in this Agreement. As used in this Agreement, "requisite remedial technology" refers to known engineering and construction practices, used or acceptable for use in the cleanup or containment of chemical contamination applicable to materials and hydrogeological conditions found at the Site, which will effectively protect the public health and environment.

(c) Olin shall be required to apply the requisite remedial technology approved by the State in accordance with the terms and conditions of this Agreement, unless, upon evidence, the Court determines that application of such technology is unnecessary to satisfy the goals described in subparagraph (a).

(d) Any judicial review concerning the application of requisite remedial technology pursuant to this Agreement shall be based on the standards and considerations described in this paragraph.

(e) For purposes of this Agreement, "chemical contamination" or "contaminants" means the presence of any of the following "listed chemicals" at or near the Site: benzene, mono-through hexachlorobenzene, pentachloronitrobenzene, tetrachloroethylene, all isomers of hexachlorocyclohexane, heptachlorocyclohexane, trichloroanisole, phenylmethyl ether (anisole), formaldehyde, mercury, chlorinated biphenyls, phenol, and di- and trichlorophenols.

(f) The State, solely at its own option but without prejudice to a claim that costs incurred in the testing may be reimbursable pursuant to paragraph 12 below, may test for additional chemicals at the Site. If the State's analysis demonstrates that chemicals other than "listed chemicals" are present at the Site and such chemicals either (i) resulted from manufacturing operations at Olin's Niagara Falls plant, or (ii) are intermixed with contaminants deposited or caused to be deposited on the Site by Olin, such chemicals shall be deemed "listed chemicals" for the purpose of subparagraph 4(e) and Appendix 6 of Plan A, which plan is described in paragraph 5, below. The State shall notify Olin of (i) the chemical(s) for which it intends to conduct additional tests, and (ii) the samples, as provided pursuant to Paragraph 7(d) of this Agreement, which it intends to so analyze, within thirty (30) days after receipt of the results of Olin's analysis of soil samples collected and analyzed pursuant to Plan A hereto, as provided for by Paragraph 5(c) of this Agreement and paragraphs I.C.3(d) and III.A of Plan A hereto. Upon such notification, the State shall retain a qualified laboratory to perform such analyses, which laboratory shall perform such analyses without unnecessary delay. The State shall promptly report the results of said analyses to Olin, and shall, within 30 days of receipt of its laboratory analyses, designate those chemicals which its analyses demonstrates are present at the Site and either (i) resulted from manufacturing operations at Olin's Niagara Falls plant, or (ii) are intermixed with contaminants deposited or caused to be deposited on the Site by Olin. Upon the State's designation of such chemical(s), Olin shall amend Plan A (and, as appropriate, Plans B-F, which plans are described in paragraph 5, below) to determine the areal and vertical extent of such chemical contamination and the appropriate remedial measures consistent with the goals set forth at paragraph 4(a) above. The State and Olin shall then agree upon new reasonable dates for the completion of the activities described in Paragraph 5, below. Olin shall not be required to begin any remedial work before the State completes its designation of other "listed chemicals" under this provision or notifies Olin that it will not designate any other chemical as "listed chemicals" under this provision.

(g) For purposes of this Agreement, the following chemicals shall be deemed to have been deposited or caused to be deposited on-site by Olin if such chemicals are found to be present at the site: hexachlorobenzene and all isomers of hexachlorocyclohexane.

(h) The presence of any or all of the listed chemicals at the Site does not constitute an admission or evidence that Olin generated or disposed of such chemicals. The State is not precluded from claiming that chemicals other than those specifically named in paragraph (e) were deposited at the Site by Olin or were reaction products of deposited chemicals.

FIELD INVESTIGATION AND REMEDIAL PROGRAM

5. Olin shall conduct a field investigation and undertake remedial work in accordance with the following provisions:

(a) Olin shall commence an initial field investigation, in accordance with "Plan A" attached hereto, according to the Schedule set out below. Implementation of Plan A shall be accomplished by appropriate personnel, approved by the State, with expertise in hydrogeology and environmental engineering. Disapproval of personnel selected by Olin shall be upon a showing of good cause by the State within 15 days after the State is given written notice by Olin of the personnel selected.

(b) Olin shall select a consultant, and the consultant shall submit to the State for approval a health and safety plan for the implementation of Plan A by May 1, 1985. The State will respond to the health and safety plan as provided in paragraph 8. The field investigation program shall commence by May 15, 1985, weather permitting, but in no event later than June ~~15~~ 24, 1985. The field investigation program, including the metal detection program, soil boring program, well installation, collection of groundwater samples, determination of groundwater levels, creek levels, etc., shall be conducted in accordance with the provisions of Plan A. The metal detection program, soil boring program, and well installation shall be concluded by September 1, 1985.

The field investigation program shall be concluded as soon as practicable, but in no event later than June 1, 1986.

(c) Preliminary data from the field investigation and sampling program described in the foregoing paragraph shall be submitted to the State as they are obtained by Olin, its contractors, or consultants in accordance with a schedule to be developed by the parties. A preliminary feasibility study of remedial options ("preliminary study") shall be submitted to the State as soon as practicable, but in no event later than December 1, 1985, unless said date is changed pursuant to paragraph 4(f) above.

(d) Olin shall submit a final report and feasibility study of remedial options ("final report") to the State as soon as practicable after data are collected which are sufficient to comprehensively evaluate the possible remedial alternatives and recommend a remediation plan alternative adequate to isolate or remove the on-site chemical contamination as provided by the goals set forth at paragraph 4(a) above, but in no event later than August 1, 1986, unless that date is changed pursuant to paragraph 4(f). Unless the final study is submitted by March 1, 1986, Olin shall submit, by March 1, 1986, an interim report identifying the additional data necessary to prepare the final report and stating the reasons the additional data are needed. The interim report shall update the evaluation of remedial options identified in the preliminary study if additional data collected since December 1, 1985, so warrant. The final report shall include all available data and results obtained during the field investigation and, except as provided by subparagraph (e), below, shall describe possible remedial alternatives and shall recommend a remediation plan alternative adequate to isolate or remove the on site chemical contamination as provided by the goals as set forth at paragraph 4(a) above. The final report shall specify the reasons for which the alternative methods of remediation identified in the final study have been rejected. Such final report or any subsequent versions of it, shall be modified if data collected after its preparation so warrant.

(e) If the feasibility study proposes containment of some or all of the contaminants on the Site as the recommended remedial plan, then the requirements of subparagraph 5(f) do not apply and Olin shall design and submit to the State a field investigation ("Plan B"), consistent with the findings of Plan A, designed to determine the extent of and potential for off-Site migration of contaminants which were deposited or caused to be deposited on-Site by Olin, unless Olin can demonstrate by clear and convincing evidence that such off-Site investigation is unnecessary to the design of a remedial plan consistent with the goals set forth at paragraph 4(a). The information gathered in the course of implementation of Plan A and Plan B shall then be used to design and submit to the State the required remediation plan for the Site ("Plan C"). Plan C shall include, at a minimum, the following elements:

(i) quarterly groundwater monitoring for 30 years;

(ii) sample collection and analysis of creek water during high and low water periods annually, and of creek sediments annually for 30 years;

(iii) establishment of an upward hydraulic gradient within the containment area, unless Olin demonstrates by clear and convincing evidence that the establishment of the same is unnecessary or inappropriate to the accomplishment of the goals set forth at paragraph 4(a) herein;

(iv) acquisition by Olin of easements which would permit the required monitoring;

(v) provisions for protection of the Site from disturbance which might increase the threat of contamination migration, including regular inspection of the Site;

(vi) provisions for the design and implementation of a contingency plan in the event that migration of contaminants occurs despite the implementation of the containment remediation plan; such contingency plan shall be consistent with the goals set forth at paragraph 4(a);

(vii) containment or removal of contaminants deposited or caused to be deposited by Olin which have migrated off-Site consistent with the goals of paragraph 4(a) above;

(viii) fiscal arrangements, guarantees, or the provision of financial assurances sufficient to ensure that Olin possesses the financial ability to perform the containment remedial plan and monitoring.

In the event that after seven years following the delivery of a Release (as described in paragraph 14(a) below) Olin demonstrates by clear and convincing evidence that conditions at the Site are such that the stated frequency or duration of the requirements set forth in the above provisions (i), (ii), or (v) are no longer necessary to a determination of whether the remediation is effective, Olin may reduce the frequency and/or duration of such monitoring or inspections. In addition, in the event that after seven years following delivery of a Release (as described in Paragraph 14(a) below), Olin is able to demonstrate that the above provision (viii) is no longer necessary to ensure performance, Olin may alter the fiscal arrangements appropriately.

(f) If the feasibility study recommends removal of contaminants from the Site, then the requirements of Paragraph 5(e) do not apply and Olin shall design and submit to the State a remedial plan consistent with that recommendation ("Plan D"). Following completion of the remedial work called for by Plan D, Olin shall design and submit to the State a plan for additional field investigations ("Plan E"), consistent with the findings of Plan A, in order to determine the extent of off-Site migration, if any, of contaminants deposited or caused to be deposited by Olin and the effectiveness of the remedial work performed. Plan E may be limited to a determination of the effectiveness of the remedial work performed if Olin can demonstrate by clear and convincing evidence that off-Site investigation is unnecessary to remediation consistent with the goals set forth at paragraph 4(a).

(g) If the information gathered as a result of Plan E reveals off-Site migration of contaminants which were deposited or caused to be deposited on-Site by Olin, Olin shall design and submit to the State a plan ("Plan F"), which is consistent with the goals of Paragraph 4 (a) above.

(h) The Attorney General, on behalf of the State of New York, shall approve or disapprove Plans B, C, D, E, and/or F pursuant to the approval mechanism set forth in Paragraph 8, and Olin shall implement the approved Plans B, C, D, E, and/or F within 60 days after approval, weather permitting.

(i) During the field investigations and remedial programs, Olin shall also implement environmental health and safety plans which shall contain, inter alia, procedures to prevent unauthorized access to the Site and to ensure the safety of persons on and/or in the vicinity of the Site during the field investigations and remedial work.

6. All proposed plans submitted by Olin shall include specific procedures for the cleansing of equipment and the disposal of contaminated materials. Said procedures shall comply with all applicable federal and state laws.

ENTRY AND INSPECTION ★ State inspection authority

7. (a) During the implementation of the field investigations and remedial programs, the State shall have authority to enter the Site or

its vicinity controlled (by easement or otherwise) by Olin during regular business hours for the purposes of inspecting and copying records, operating logs, contracts, or other documents or property required to assess Olin's compliance with this Agreement. Olin shall also allow the State to inspect all other property related to the implementation of this Agreement and to inspect and copy all records, operating logs, contracts, or other documents (so long as such property and documents would be subject to inspection and discovery pursuant to Rule 34 of the Federal Rules of Civil Procedure; provided, however, no party shall have been deemed to waive any privilege available under New York State and federal law) which the State requires to assess Olin's compliance with this Agreement. Olin shall honor all reasonable and timely requests for such entry or inspection by the State conditioned only upon presentation of proper credentials and prior written notification to Olin or its agent (as designated pursuant to Paragraph 9) of the purpose of said request.

(b) Olin shall identify to the state all laboratories, whether or not owned by Olin, participating in the performance of the requirements of this Agreement. To the extent provided in and in accordance with Paragraph 7(a), the State may enter and inspect any such laboratory owned or operated by Olin or any subsidiary of Olin and inspect and copy all records located therein required to assess Olin's compliance with this Agreement; in addition, Olin shall consent to the State obtaining such access to laboratories owned by third parties.

(c) The State shall have the right to designate an agent or agents having appropriate qualifications and education in environmental engineering, chemistry, or hydrogeology to participate in and assist, on and off the Site, in the field investigations and remedial programs. These agents and Olin or its agents or consultants shall confer on a timely basis and cooperate in the accomplishment of the programs' goals and purposes. The State's agents shall be permitted access to the Site and its vicinity controlled by Olin whenever any aspect of a program is being performed or studied.

(d) Where possible, any samples collected by Olin shall be sufficiently large in quantity to allow for the provision of split samples to the State. Olin shall advise the State of any sample collection at least 48 hours before samples are collected except when such notice is not possible; if such notice cannot be given, notice of sample collection shall be given as soon as possible. Soil borings shall be archived as provided in Plan A and will be split with the State as soon as is practicable after Olin selects samples for analysis as provided in Plan A.

SUBMISSION OF PLANS

8. The parties shall proceed as follows whenever this Agreement requires Olin to submit a proposed plan for the State's approval:

(a) The State, through the Attorney General, shall determine whether each proposed plan is in accordance with the applicable purposes and goals of this Agreement.

(b) Throughout the review process, the parties shall attempt in good faith to resolve any differences regarding an appropriate and acceptable plan.

(c) After receiving a proposed plan, the State shall promptly respond to said proposal. If the proposal is complete and acceptable, the State shall serve written notice of approval to Olin within 30 days after receipt of the proposal. The plan shall become effective on the date the acceptance is served upon Olin.

(d) If the proposal is not complete or acceptable, the State shall serve a written notification of disapproval within 30 days after receipt of the proposal which shall include its particular objections and may include suggested modifications. If the parties cannot agree upon a proposed plan within 30 days of the notice of disapproval of a proposed plan, the State, through the Attorney General, shall present Olin with a plan which shall be implemented by Olin unless Olin moves the court within 15 days after receipt of the State's plan for a determination that the implementation of the State's plan is unreasonable in light of the goals and purposes of the Agreement. On the basis of the Court's determination, the Court may issue any order appropriate to effectuate the purposes and goals of this Agreement.

(e) In each instance in which a plan as proposed or modified becomes effective, the State shall attach it to this Agreement as an appendix, serve copies of the appended document on Olin and file it with the Court in accordance with all other filing requirements set forth herein.

(f) Whenever Olin is required to make significant submissions to the State, Olin shall make a simultaneous and identical submission to Zito and Batrouny or their legal representatives. Zito and Batrouny shall promptly inform the State of their comments, concerns or objections concerning the proposed plan. The State shall take Zito's and Batrouny's comments, concerns and objections into account in determining whether the proposal is complete and acceptable.

NOTIFICATION

9. Any documents which Olin, Zito, or Batrouny are required to send to the State, pursuant to this Agreement, shall be sent to:

(a) GLEN BAILEY
New York State Department of Environmental Conservation
600 Delaware Avenue
Buffalo, New York 14202

(b) GORDON J. JOHNSON
Assistant Attorney General
Environmental Protection Bureau
New York State Department of Law
Two World Trade Center
New York, New York 10047

(c) GREGORY SHKUDA
Department of Law
Two World Trade Center
New York, New York 10047

Any documents which the State, Zito, or Batrouny are required to send to Olin pursuant to this Agreement shall be sent to:

(d) GEORGE H. PAIN
Counsel
Olin Corporation (3-J)
120 Long Ridge Road
Stamford, CT 06904

(e) VERRILL M. NORWOOD
Vice President, Environmental Affairs
Olin Corporation
P.O. Box 248
Lower River Road
Charleston, TN 37310

(f) DANIEL M. DARRAGH
RICK W. KENNEDY
Hodgson, Russ, Andrews, Woods & Goodyear
1800 One M&T Plaza
Buffalo, NY 14203

Any documents which Olin or the State are required to send to Batrouny and Zito, pursuant to this Agreement, shall be sent to:

(g) JOEL E. SCHWEITZER
(for Batrouny)
Gellman, Brydges, Schroff & Schweitzer
M.P.O. Box 279
Niagara Falls, NY 14302

(h) STANLEY GROSSMAN
(for Zito)
Grossman, Levine & Civiletto
331 Buffalo Avenue
Niagara Falls, NY 14302

Any of the persons receiving documents may designate in writing a substitute to whom documents will be sent instead.

DELAY OR PREVENTION OF PERFORMANCE

10. (a) Olin and the State shall use their best efforts to minimize or avoid any delay or prevention of the performance of their obligations pursuant to this Agreement. If any event occurs which delays or prevents, or leads Olin to anticipate delays or prevention of, Olin's compliance with any appropriate term or condition of this Agreement, Olin

shall promptly so notify the State. As soon thereafter as possible, but in no event later than 20 days after learning of such delay or prevention, Olin shall submit a written statement to the State which shall fully describe the anticipated cause of such delay or prevention, the anticipated length of the delay, the actions Olin has taken, and proposes to take, if any, to minimize the delay and to mitigate the impact of such event, and the schedules of such actions.

(b) To the extent that events which delay or prevent Olin's compliance with any appropriate term or condition of this Agreement have been caused by "force majeure," e.g., an act of God which makes it impossible to perform, and Olin has complied with the notification provision provided in subparagraph (a), the time for such performance hereunder shall be extended for the time period of such delay and if such circumstances prevent such performance, such performance shall be excused unless and until circumstances so change that the performance is no longer prevented; provided, however, that any excused delay or prevention of any intermediate requirement shall not result in the excused delay or prevention of any subsequent requirement if the subsequent step can reasonably be implemented without completion of the prior step.

(c) Reasonably foreseeable increases in costs or expenses associated with the implementation of actions required by this Agreement shall not, in any event, be a basis for extensions of time, excuses of performance, or defenses to a petition for sanctions. Any excused delay or prevention of performance predicated upon unforeseeable increases in costs or expenses shall not result in the excused delay or prevention of performance of any other requirement which reasonably can be implemented notwithstanding such unforeseeable increases or which reasonably can be modified to take into account such unforeseeable increases, consistent with the goals of Paragraph 4(a). If the performance of an action required by this Agreement is excused on the basis of unforeseeable increases in costs or expenses, such excusal shall not constitute a defense to any claim made or action brought by the State for injunctive relief or for reimbursement of costs it may have incurred performing any such excused action. Increases in costs or expenses resulting from (a) the designation of chemicals, other than those named at paragraph 4(e) of this Agreement, as "listed chemicals" pursuant to paragraph 4(f) of this Agreement, or (b) implementation and performance of a health and safety plan, in connection with each field investigation and remediation plan required pursuant to paragraph 5 of this Agreement, which health and safety plan is necessary to protect the public and the environment from chemical contamination that may otherwise occur in the course of performing any field investigation remediation, are reasonably foreseeable.

(d) If the State and Olin agree that the delay or prevention is excusable under the criteria set forth in subparagraph (b) and agree concerning the length of such delay or prevention, Olin and the State shall file with the Court a stipulation and proposed order to such effect. If, however, within 10 days after Olin's written statement to the State, the State and Olin do not so stipulate or the State advises Olin in writing that it does not consider the aforementioned circumstances to have been satisfied or does not agree with the length of the delay, the State may immediately advise the Court of any delay or prevention, or anticipated delay or prevention, of Olin's performance of its obligations pursuant to this Agreement. Thereafter, either the State or Olin may submit the matter to the Court for resolution.

PERMITS AND EASEMENTS

11. (a) Olin shall use its best efforts, and the State shall cooperate consistent with its legal authority, to obtain on a timely basis, such permits, easements, rights of way, rights of entry, approvals, or other authorizations from any federal, State, or local government entity, or any corporation, partnership, association, or private person which are necessary to carry out any of Olin's obligations pursuant to this Agreement. Olin shall promptly notify the State in the event of Olin's inability to obtain such authorizations on a timely basis or its inability to obtain authorizations which do not contain use restrictions which prohibit or interfere with activities required pursuant to this Agreement, or of Olin's receipt of governmental authorizations containing terms or conditions not specifically required by federal or state statutes or regulations.

(b) In the event Olin is unable to obtain the authorizations required by the preceding paragraph, the State shall, consistent with its legal authority, assist in obtaining, as appropriate, all such authorizations which Olin was unable to obtain or which it could not obtain without terms and conditions which effectively prevent implementation of this Agreement. If, despite Olin's best efforts, Olin does not obtain the aforementioned authorizations on a timely basis or if Olin obtains authorizations containing terms and conditions which effectively prevent timely compliance with the terms and conditions of this Agreement, the time for performance of any obligations pursuant to this Agreement which are necessarily dependent upon such authorizations shall be extended as appropriate. If, despite Olin's best efforts, such authorizations or access cannot be obtained despite an enlargement of time, this Agreement may be modified by excusing performance of any obligations pursuant to this Agreement which are necessarily dependent upon such authorizations.

(c) In no event shall the State be required to exercise its powers in order to obtain the easements described by paragraph 5(e)(iv), and Olin's failure to obtain such easements shall not constitute a basis for excusing performance.

REIMBURSEMENT

12. The term "reimbursable costs" as used in this Agreement, shall mean those costs incurred by the State which the State is legally entitled to recover under the Comprehensive Environmental Response, Compensation and Liability Act, the New York State Environmental Conservation Law and the common law of New York and which are (i) reasonable and (ii) not duplicative of costs previously incurred by the State and reimbursed by Olin.

(a) Payment of past costs.

In order to expedite the execution of this Agreement, and without admitting that any of the costs incurred by the State before the date of execution of this Agreement are reimbursable costs, Olin shall pay to the Hazardous Waste Remedial Fund (established by the New York State Finance Law section 97-b) the sum of $26,371.31 within sixty days of the effective date of this Agreement. Upon receipt of said sum, the State shall execute and deliver a release of liability to Olin for all claims resulting from or relating to all costs related to the Site incurred by the State or its agent prior to the date of execution of this Agreement.

(b) Periodic payment of reimbursable costs.

Commencing six (6) months from the date this Agreement is executed and every six (6) months thereafter, the State shall submit to Olin a detailed statement of the reimbursable costs incurred during the preceding six months. The Statement shall be sufficiently detailed and documented to allow Olin to assess whether the costs claimed by the State to be reimbursable costs satisfy the criteria set forth in subparagraph (a). The statement shall be submitted to Olin as soon as is practicable after the end of the six month period which it applies. Within sixty (60) days of receipt of the statement, Olin will either pay the sum set forth in the statement or notify the State in writing of its objection(s) to it. If the objection(s) cannot be resolved by the parties within thirty (30) days, the State may move the Court for a determination of the amount of reimbursable costs owed for the six month period in dispute.

FINANCIAL SECURITY

13. (a) If at any time prior to the completion of Plans A through F (i) the consolidated net worth of Olin declines by twenty-five percent (25%) or more in any one fiscal quarter, or (ii) over a period of three consecutive fiscal quarters the consolidated net worth of Olin declines by a total of twenty-five percent (25%) or more as compared with the consolidated net worth of Olin as of the beginning of the first of such quarters, or (iii) if the consolidated net worth of Olin declines by twenty-five percent (25%) or more in any one fiscal year, or (iv) if the consolidated net worth of Olin declines at any time to one hundred million dollars ($100,000,000) or below, Olin shall immediately notify the State and shall promptly provide security in an amount equal to one hundred and twenty-five percent (125%) of the estimated cost to complete the implementation of the field investigation and remedial plans.

(b) Notwithstanding the foregoing, if because of other circumstances affecting the financial conditions of Olin, the State determines that other or additional financial security is necessary, the State may seek such relief from the Court which shall grant such relief if necessary to insure the availability of funds to complete the implementation of field investigations and remedial plans described in paragraph 5, above.

MISCELLANEOUS PROVISIONS

14. (a) Upon either (i) certification by the State that Olin has completed satisfactorily, in accordance with the goals of the Agreement stated in Paragraph 4(a), the remedial plans required by Paragraphs 5(f) and (g), or (ii) certification by the State that Olin has implemented satisfactorily, in accordance with the goals of Paragraph 4(a) herein, the remedial plans required by Paragraph 5(e) and is performing the monitoring required thereby, the State will execute and deliver a Release of Liability ("Release") to Olin for the following claims:

(i) All claims for civil penalties which were raised or could have been raised in this Action;

(ii) All other claims resulting from or relating to any migration, discharge or release of chemicals or other substances from the Site and all other claims which were raised in this Action, except claims resulting from, or relating to, any migration, discharge or release from the Site of chemicals or other substances occurring after the date of the Release.

Certification of remediation, or the reasons for denial of such certification, shall be delivered in writing by the State to Olin within thirty (30) days after Olin's written request for such certification. If the State denies certification and the parties cannot in good faith resolve the disagreement within thirty (30) days from date of denial, Olin may move the court for an Order directing that the State provide such certification. Olin shall be entitled to said Order if Olin demonstrates that it has either: (i) completed satisfactorily, in accordance with the goals of the Agreement stated in Paragraph 4(a), the remedial plans required by Paragraphs 5(f) and (g); or (ii) implemented satisfactorily, in accordance with the goals of Paragraph 4(a), the remedial plans required by Paragraph 5(e) and is performing the monitoring required thereby.

(b) This Agreement does not affect any other claims or actions the State may have now or in the future against Olin or any other person.

(c) Nothing herein precludes the State from enforcing any legal or equitable rights or claims whatsoever which it may have now or in the future against anyone other than Olin.

(d) Nothing herein precludes the State from enforcing any legal or equitable rights or claims whatsoever which arise from activities of Olin after the date of the Release.

(e) Nothing herein discharges or releases Olin from any obligations at law or in equity which arise from pollution of soil, groundwater and drinking water which is unrelated to the chemical contamination which is the subject of this Agreement, unless said pollution is identified by Olin in its field investigation conducted pursuant to Paragraph 5 herein and addressed in Olin's remedial plan pursuant to said Paragraph.

(f) Until the Release is given, compliance with the provisions of this Agreement shall be considered a complete defense to the Action or any other action the State may hereinafter bring against Olin which arises out of or relates to the migration, discharge, or release of contaminants from the Site which migration, discharge, or release is or reasonably should have been known by the State to be occurring or existing as of the date of the Agreement. Nothing herein shall limit the authority of the State or its agencies to order and require Olin to respond to emergencies which constitute an immediate and substantial endangerment to the health and safety of people or to the environment arising from the migration, discharge, or release from the Site of contaminants deposited or caused to be deposited by Olin on the Site.

(g) Nothing herein shall be deemed to waive or release any claims on behalf of Zito or Batrouny against Olin for damages to persons and property which may have resulted from contaminants deposited or caused to be deposited at the Site by Olin.

15. There shall be the following filing requirements:

(a) Within fifteen days after the effective date of this Agreement, the State may file a copy of this Agreement with the Niagara County Clerk to be recorded against the parcels of land which include some or all of the Site;

(b) Within fifteen days after the effective date of any plan approved pursuant to this Agreement, the State may similarly file a copy of the resulting appended version of this Agreement;

(c) Within fifteen days after obtaining an easement pursuant to paragraph 11 of this Agreement, Olin or the State shall file a copy of such easement for recording; and

(d) Within fifteen days of the certification by the State that Olin's remedial program has been successfully completed and that the goals of this Agreement have been met, the State and Olin shall, if notices have been filed pursuant to subparagraphs (a), (b), and (c), also file a notice with the Niagara County Clerk that this Agreement has been fully implemented, to be recorded against all parcels against which a notice has been recorded before.

(e) All property, including real property structures, constructions, and fixtures, owned by Site owner or owners ("Owners") at the site may be freely alienated; provided that forty-five (45) days prior to the date of such alienation the Owners give the State written notice of such alienation and a description of which of the Owners' obligations, if any, pursuant to the Agreement shall be performed by the person or entity to whom the property is alienated. The Owners may proceed with such alienation unless, within 30 days following such notification (i) the State or Olin file a petition with the Court objecting to such alienation on grounds that it would interfere with the performance or any party's obligations pursuant to this Agreement and (ii) in response to such petition, the Court orders such alienation not to proceed pending final determination of the issues raised by such petition or the Court determines that such alienation would interfere with a party's obligations pursuant to this Agreement. In the event of such alienation, all of the Owners' obligations pursuant to this Agreement shall continue to be met either by, at the Owners' option, the owners or the person or entity to whom the property is alienated. Any deed, title or other instrument of conveyance of property at the Site shall contain notice of such provisions for continuing performance as herein above described and, additionally, shall clearly describe the use for which the property has been subjected.

(f) Owners and any subsequent owners shall comply with the provisions of §27-1317 of the New York State Environmental Conservation Law and nothing herein constitutes a waiver of the prov'-ion of said law.

16. The effective date of this Agreement shall be the date on which it is approved by the Court.

17. The provisions, terms and conditions herein shall bind Olin, its successors and assigns.

18. The terms and conditions of this Agreement shall include the terms and conditions of any plan appended to this Agreement pursuant to the provisions herein.

19. The Court shall retain jurisdiction to modify and enforce the terms and conditions of this Agreement and to resolve all disputes arising hereunder as may be necessary or appropriate for the construction or execution of this Agreement. In order to assist the Court in resolving technically complicated and complex issues which may hereinafter be presented to it in this Action, any party hereto may petition the Court, pursuant to Rule 53 of the Federal Rules of Civil

Procedure, to refer such issues, as appropriate, to a master.

20. All information and documents submitted by Olin to the State pursuant to this Agreement shall be subject to public inspection except such information which the Court, upon application and demonstration by Olin, finds is a trade secret disclosure of which would cause substantial injury to the competitive position of Olin.

21. Neither this Agreement nor any part hereof shall constitute an admission of law or fact or evidence of same, nor of any violation of any law or regulation. The parties hereto may not rely on this Agreement in any other action or proceeding. It is intended that this Agreement shall neither create nor affect the rights of persons or entities who are not parties to this Action.

22. This Agreement shall bind and inure to the benefit of all the parties hereto and their respective successors and assigns.

23. This Agreement may be executed in counterpart. Each counterpart may serve as a duplicate original.

24. The persons signing this agreement represent that they have full authority to bind the respective parties which they represent.

The State and Olin, by their duly authorized representatives, and Zito and Batrouny consent to this judgment on _______ day of March, 1985.

THE STATE OF NEW YORK

By: ______________________
Albert M. Bronson

Title: ______________________

By: ______________________
Gordon J. Johnson

Title: ______________________

By: ______________________
James A. Savinsky

Title: ______________________

OLIN CORPORATION

By: ______________________
J. W. Johnstone

Title: Executive Vice President

____
JOHN ZITO

____
ELIZABETH ZITO

____
ARTHUR BATROUNY

____
BEVERLY JANE BATROUNY

The foregoing Consent Judgment, with Plan A incorporated therein and attached hereto, is hereby adopted and enforced in this cause, The State of New York v. Olin Corporation, et al., Civil Action No. CIV 83-1400, this _________ day of _______________, 1985.

____

United States District Judge

Plan A

PINE/TUSCARORA INVESTIGATION PLAN

I. REMEDIAL INVESTIGATION

A. GROUND SURVEY

A preliminary site map will be prepared from existing information (scale 1 = 20') which will provide an overall site description. Buildings, power lines, buried pipelines, and other physical or geopolitical landmarks will be noted. This map will serve as the working, field base map. The borehole grid will be laid out on this preliminary map. In addition, as field work progresses, various appropriate notes may be made for incorporation in a final site map.

B. BURIED METAL DETECTION

1) Purpose

a) To detect location of any buried metal drums.

b) To define buried metal obstructions on-site as potential avoidance areas for drilling operations.

2) Instrumentation

a) Function

1) Fisher M-Scope Model TW-5 metal detector

2) Senses buried metal by transmission of radio field and detecting field distortions caused by metal presence.

3) Functions by traverse over ground surface.

4) Traverses cover 4-foot width, with series of traverses across site to cover entire site area.

b) Limitations/capabilities

1) Will detect presence/absence of buried metal

2) Will not detect shape of buried metal

3) Will not be affected by presence of on-site automobiles.

4) Can be marginally affected by presence of powerlines, correctable by calibration.

5) Can detect metal several inches in size.

6) Depth of detection up to 20 feet depending on soil conditions.

7) Operation of unit is described in attachment.

3) Field Procedures

a) Area of concern for metal detection is entire site except those areas to the south and west of the Batrouny residence, motel and garage have been excluded because they contained structures or were at grade elevation at the time of disposal. (Area to the east of the garage is included in metal detection survey). See Appendix 2.

b) Clear site of parked automobiles to facilitate traverse of metal detector.

1) Tow truck will move autos to south end of site to allow room for drilling and metal detection traverse.

c) Linear traverse lines will be laid out by pegged cord

1) Line will allow 3-foot wide traverse corridors across width of site.

2) This corridor width will allow small overlap between adjacent traverses.

3) When buried metal is detected, marker stakes will be placed to define the location and extent of buried metal, immediately after detection.

4) Buried metal pipelines will be defined in like manner.

5) Where buried pipelines are evident, a secondary traverse will be made to verify its presence along the pipeline length.

6) This secondary traverse may cross initial traverse pattern diagonally.

7) Secondary traverses will be done for all buried metal pipelines.

8) Secondary traverses will also be made to verify the aerial perimeter of any other detected metal.

9) All pipeline and buried metal locations will then be plotted on baseline map of the study area and will be included in any reports on the study.

4) Results

a) Metal detection investigation will have established the perimeter of any buried metal.

b) Metal detection will define buried pipelines.

c) This will identify an area for avoidance by drilling apparatus, i.e., avoidance area will be the area underneath the powerline plus an area 10 feet wide centered on the buried pipelines.

C. BORING PROGRAM

1) Purpose

a) To visually note presence of any buried waste materials and determine the area and depth of their occurrence on-site.

b) To identify as best as possible the buried waste materials are.

c) To collect soil samples for analysis.

2) Field Layout

a) The study area will be divided into a grid by wooden field stakes.

b) Grid points will be 50 feet apart.

c) Study area is the total site minus the agreed upon exclusion areas noted on base map (Appendix 2).

1) These exclusion areas include the strip of land defined as the powerline R.O.W. (detected in buried metal detection program) and is noted in attached letter, dated January 4, 1982. (Appendix 3)

2) Study area is bounded on east by Cayuga Creek, on north by Cayuga Creek and the Batrouny property line, on west by a line parallel to and 10 feet from the east side of Batrouny house and motel, and on south by a line 10 feet from and parallel to rear of the garage; however the area to the east of the garage shall be sampled according to Section I.C.(2)(e)(1).

3) If waste is encountered in the course of study at the edge of the study area, the study area shall be expanded in order to determine the extent of buried waste.

d) All grid points will be numbered by row and column to identify any samples collected at each point. Grid point number~ will be marked on stakes and on field maps.

e) There will be a total of about 35 (±) borings.

1) Initial grid at 50-foot centers is shown on sketch (Appendix 2) and involves 25 (±) borings, including one boring east and south of the garage.

2) An additional 10 (±) borings may be sited in the field to define the extent of any burial zones detected by the initial 25 borings. <u>If additional study is necessary to define the waste areas in the R.O.W., small test pits may be utilized if borings are not feasible.</u> For the purpose of Plan A, "small" means the width of a standard backhoe blade. Soils from test pits will be treated in the same manner as auger cuttings as provided at 3(c)(4).

3) The additional 10 borings will be sited by judgement of the Olin field engineer, consistent with Section II, based upon visual inspection and aerial distribution of any buried waste as noted in core samples from the 25 initial borings.

f) All samples taken during the study will be numbered according to grid location and depth below grade to provide consistent reference to any sample locations.

3) Boring and Sampling Procedures

a) Continuous core samples will be taken.

1) Where buried waste is encountered, samples will be collected to one foot into virgin soil.

2) Boring will be terminated when no buried waste is found one foot into any aquiclude encountered below fill. For the purposes of this study, an aquiclude is a poorly permeable formation or bed that impedes groundwater movement.

3) Should a soil boring be terminated in a clay stratum less than three feet thick, an impervious grout plug will be tremied into the bottom of the boring to create an impervious grout seal. If the clay stratum is greater than three feet thick, a sufficient quantity of bentonite pellets shall be placed down the boring to provide a seal against downward migration.

4) Presence/absence of waste to be determined by onsite visual inspection and, concurrent with boring, scanning of samples with an organic vapor meter (OVM) by the inspection field engineer, consistent with Section II.

5) Four soil borings at the corners of the study area shall be completed to bedrock, provided that the borings can be located in non-waste areas. These borings may be omitted if reliable geological information regarding bedrock elevation and stratigraphy across the site is otherwise available.

6) A log of all cores will be kept by the field geologist identified numbered by grid location and depth of core sample as well as core sample description. The log will include information such as names of the boring crew, date, location, initial water table, soil descriptions, blowcounts, and presence/absence of waste. The field log will be considered preliminary information subject to refinement by consultation with other profes ionals, laboratory analyses and tests, etc.

7) If concrete is encountered at very shallow depths, small test pits will be necessary in this area. Samples will be appropriately collected to yield the same information as borings.

b) Drilling and core sampling methods

1) Drilling and sampling will be done by hollow stem auger and split spoon core sampler.

2) The split spoon sampler will be cleaned between advances by wire brushing and washing/flushing in a bucket of water, washed with detergent, rinsed with distilled water, solvent rinsed, then air dried. Spent solvents and rinse water will be stored and disposed of in accordance with applicable regulations.

c) Auger cuttings and completed boreholes

1) Seven selected boreholes will be converted to groundwater monitoring wells. Excess auger cuttings and excess groundwater from development will be stored and disposed of in accordance with applicable regulations.

2) Auger cuttings (from borings not converted to monitoring wells) will be poured back down the boreholes to a depth of two feet below grade with the remainder of the boreholes packed with impervious grout. A six-inch space between grout and surface level shall be left and clean fill deposited to surface level.

3) Should a soil boring be terminated in a clay stratum less than three feet thick, an impervious grout plug will be tremied into the bottom of the boring to create an impervious grout seal. If the clay stratum is greater than three feet thick, a sufficient quantity of bentonite pellets shall be placed down the boring to provide a seal against downward migration.

4) Soil from test pits may be replaced to within six inches of grade and clean fill then deposited to grade.

d) Samples for laboratory permeability

1) Special sampling procedures will be used to collect samples for laboratory permeability measurements as described below.

2) Six selected samples will be collected in the field based upon judgment by Olin field geologist, consistent with Section II.

3) Samples will be collected by Shelby Tube, a method similar to split spoon, but consisting of a solid metal tube driven into soil, sealed with wax upon withdrawal and sent to laboratory in that form for permeability tests.

4) This method preserves the sample in an undisturbed state with natural moisture content and texture for accurate permeability tests.

5) This method can replace split spoon tests for the six specific samples at any grid point or depth.

6) The State may have representatives on hand when Shelby tubes are opened.

7) After permeability testing, the soil contained in the Shelby tubes should be preserved for possible chemical analysis.

4) Handling Core Samples

a) Each core sample will be removed from the split spoon and stored in a clean glass jar with Teflon lined lid, and cover-sealed with a paper label.

b) Each jar will be marked with sample number consisting of grid point and depth of core, sampler, time and date of collection.

c) Sample will be visually inspected and logged in the field.

1) For soil, texture and soil classification will be noted.

2) For any waste, description of waste will be noted, i.e., color, organic vapor level and texture.

d) Twenty samples selected by the field engineer, consistent with Section II will be analyzed as detailed in analytical protocol outline.

1) Selection will be made after reviewing boring logs and visual inspection at laboratory. The field engineer(s) who supervised the taking of the samples shall participate in the sample selection.

2) Selection will be done so as to include samples of any and all different wastes found on the site, and shall also include seven soil samples taken from the intervals selected for well screen placement.

3) If the analysis of the 13 non-well borehole samples is no longer sufficient to define and characterize the waste areas, up to seven additional samples shall be analyzed to sufficiently characterize the waste areas.

e) All samples will have chain-of-custody label attached to bottle and will be handled according to chain-of-custody procedures described below.

f) All samples will be shipped to analytical laboratory as per U.S. Department of Transportation (USDOT) procedures governing the shipping of potentially hazardous substances (49 CFR 272.101).

g) All samples will be maintained at 4°C during shipment, as specified in 49 FR 43260. (Appendix 4)

h) All samples will be stored appropriately at the laboratory for the maximum recommended periods as provided for in the appendices, so that additional future analyses can be performed if found necessary.

5) Chain-of-Custody Procedures

a) Purpose: To establish a chain of responsibility for possession and integrity of sample at each point of transfer and exchange from collection to analysis.

b) Labels will be attached to each sample bottle and will identify location, sample number, date and time of collection, collector(s). The chain-of-custody document will identify the handlers (including commercial shipper), receiver at analytical laboratory and all other handlers at laboratory, up to time of analysis. All such receivers and handlers will sign the chain-of-custody document. The bill of lading from the commercial shipper may be substituted for the shipper's signature. Analysts will sign laboratory report sheets and/or notebooks.

c) Chain-of-custody labels will be returned to Olin field engineer upon analysis of sample for cross-check in field log book.

d) All sample containers will have a paper label which will be broken only immediately prior to analysis.

e) Each sample received by laboratory will be logged in by sample number, date of receipt, and date of analysis and analytical results.

f) All analytical results will be signed by appropriate personnel at laboratory.

D. GROUNDWATER PROGRAM

1) Purpose: To collect samples of groundwater for analysis, measure water table depth and gradient.

2) Seven selected boreholes will be converted to groundwater monitoring wells.

a) The locations of wells will be selected to allow distribution across the site for vertical and horizontal groundwater table measurement and sample collection.

Location of wells will be made by the field geologist consistent with Section II.

b) The boreholes will be converted as follows:

1) As the borehole is completed, soil samples will be taken by split spoon sampler and hollow stem auger, detailed in previous section. The borehole will not be backfilled.

2) A galvanized steel well casing will be lowered into the hollow stem auger to bottom of the hole.

3) The hollow stem auger will then be removed from the hole around the well casing, leaving the well casing in place.

4) Auger cuttings will be retained and disposed of as specified in I.C.3.c.(1).

5) No well will be located in waste areas.

6) If groundwater table is below the expected 10-foot depth below grade, the selected boreholes may be drilled deeper so as to allow for collection of groundwater samples. These borings will extend down to but not through the aquiclude.

7) Selection of wells to be drilled deeper and depth of drilling will be at the judgment of the Olin field geologist consistent with Section II, and will be logged in his field log book.

8) Wells will be installed at the surface of any aquiclude, e.g., native clay stratum that is encountered below the fill. This aquiclude will be

defined in the field by the Olin field geologist consistent with Section II.

3) Well Construction

a) The portion of the well casing below water table will be screened to allow in-flow of groundwater.

b) Screen will extend one foot above water table to safely allow for any seasonal fluctuations of water table levels. It will extend below water table to the aquiclude defined above.

c) Screen will be five foot lengths of .010-inch slot stainless steel, casing will be galvanized steel, two inches in diameter, with flush joint couplings and lockable vented caps. Pipe dope and/or lubricants will not be used.

d) The annular space (between casing and hole wall) will be backfilled with clean gravel or coarse sand (3-10 Tyler mesh) fill approximately one foot above the top of the well screen to minimize suspended sediments reaching the well.

e) At the top of the gravel pack a one-foot thick impervious bentonite plug will be set, and from there to above ground level, an impervious bentonite grout mixture will be set. This will ensure that no surface run-off directly enters the well and that only groundwater is sampled.

f) The top of the casing will extend two to three feet above ground level unless otherwise specified by the property owners in the site access agreements.

g) A protective four-inch casing will be placed around the two-inch well casing above ground level. A concrete collar will be poured around the four-inch casing for further protection. Each well will be clearly labeled and noted on the site map.

h) All well caps will be lockable and kept locked. The Olin field geologist will retain the keys. Spare keys will be kept on file at the office of the geologist.

i) Keys must be signed out and in, and only used by the signer. Purpose of key sign-out must be stated. The State will have access to the keys upon 24 hours notice. Access to the wells will normally be for the purpose of taking samples or making water table measurements. Access to the wells shall be restricted, where practicable, to times that do not interfere with Olin's field program.

4) Upon completion of the boring program and well installation, the site will be surveyed and maps will be prepared by a licensed surveyor. Said survey maps shall detail physical and legal property boundaries, surface contours, locations of buildings and structures, buried pipelines and powerline R.O.W.'s, well and boring locations and elevations of wells to the nearest .01 foot in relation to mean sea level. A contour map of virgin soil elevations and waste locations shall also be prepared.

5) Well Development

a) Wells will be blown with compressed air until clear water is produced, and then pumped to remove three well volumes. After three well volumes are removed and three consecutive identical conductance readings are obtained during a three minute interval, the wells will be considered developed.

b) How can you be sure that what you are reading is right.

6) Water Table Measurement

a) The top of each well casing will be marked and measured, referenced to USGS datum. A marker on Pine Avenue bridge and an upstream point from which the relative elevation of creek water in Cayuga Creek can be measured will also be marked and measured, referenced to USGS datum.

b) Well top elevations will serve as reference points for water table measurement in each well.

c) Water table levels will be measured to the nearest .01 foot from casing top by one of several methods: (1) a weighted measured tape which will sound when it touches water level; or (2) an electric probe on a measured line which will light a small bulb or move a chart needle at surface when the probe hits water (conducting a small current).

d) All well depths, pipe top elevations and creek level elevations will be recorded by an Olin field technician, to .01 foot at 30 to 35-day intervals for one year after the first measurement is taken. At least a 48-hour notice will be provided to the State prior to the measuring date.

e) Data will be used to plot groundwater table gradient and the relation of water table to creek level. Separate high and low water contours will be plotted if differences are significant.

7 6) Groundwater Sampling

a) Water will be flushed from wells by a peristaltic pump with silicone rubber interior tubing. Precautions will be taken to insure removal of the entire column of stagnant well casing water. All down hole tubing will be of inert plastic and will be well dedicated. Pump will be repeatedly rinsed with distilled water between wells. Inert plastic will be disposed of after each sampling.

b) All wells will be flushed prior to sampling by extracting three times the volume of well casing (at first sampling, after five times the volume), or once to dryness if recharge is slow; and sampled after three identical specific conductance readings are obtained within a three minute interval.

c) All flushed water will be retained and properly disposed of in accordance with regulatory requirements.

d) Samples will be collected monthly for first three months and quarterly thereafter. First sampling will be done at least two weeks after well development and in any event as soon as practicable after the analytical results of the soil sampling are complete. Groundwater samples will be collected by hand bailing to insure that no air contacts the samples thereby potentially volatilizing any chemical constituents of the sample.

e) If well recovery (fill-up after water withdrawal) is slow, sampling of all wells shall occur over one day under rising head conditions.

f) Caps will be locked after completion of each sampling.

g) Samples will be collected in glass bottles with Teflon-lined lids, and sealed with a paper seal.

h) Groundwater sampling procedures will follow the principles delineated in 1) "Procedures Manual for Groundwater Monitoring at Solid Waste Disposal Facilities" (USEPA SW-611) Dec. 1980 and/or "Handbook for Sampling and Sample Preservation of Water and Wastewater", (EPA-600/4-82-029) September 1982.

8) Handling of Groundwater Samples

a) Samples will be maintained at 4°C during shipment to the laboratory according to procedures detailed in soils sampling section of Boring Program. Sealed insulated coolers with "cooler paks" will be used for storing and transporting samples to the analytical laboratory.

b) Chain-of-custody procedures, as detailed in Boring Program will also apply to all groundwater samples.

9) Field measurement for lateral permeability. Well pump down recovery rate tests will be conducted in four wells to determine the permeability of the saturated aquifer in accordance with procedures in Appendix 5.

II. COOPERATION WITH THE STATE

A) The field engineer(s) and geologist(s) shall confer with the State's on-site representative who shall have the right to advise concerning the propriety and correctness of field decisions. All field personnel shall make good faith attempts to resolve disputes concerning methodology, boring location, sample collection and other matters requiring in-field judgment. If dispute resolution fails, and it subsequently is determined that action taken was erroneous, necessary corrective action shall be taken by Olin. Both parties shall maintain the right to request the immediate cessation of any procedure, work or action, which it considers to be unsafe or a health hazard to those on the site or its environs.

B) Soil samples collected by Olin shall be sufficiently large to allow for the splitting of samples with the State. The State shall be provided split samples upon its request. Selection by the State of soil samples need not be made until analytical results from the water samples have been provided to the State. The State shall be allowed splits of water samples at the time of sampling.

III. ANALYTICAL PROTOCOL

A. SOILS

1) Sample parameters and procedures

   a) Analysis one time on 20 samples, two replicates for each sample.

   b) Analyze for HCB and BHC in all samples.

   c) At the time of collection all core samples will be examined visually and with an OVM to detect samples which are suspected to be other material than BHC and HCB.

   d) Of these visually and organic vapor examined core samples, select up to 10 representative samples for each suspected waste and analyze for the list of potential Olin contaminants (Appendix 6 and paragraph 4(e) of the Consent Decree).

   e) Measure moisture content of soil samples to facilitate chemical analysis reporting on a dry basis.

2) Sampling handling and analysis

   a) Portions for analysis from each core will be taken from the core center to eliminate the potential of core surface contamination.

   b) Volatile priority pollutants in soils will be analyzed according to the attached procedure - Method 8240 in USEPA SW-846. (Appendix 7).

   c) Base/neutral pesticide and acidic samples will be prepared for organic analysis by extraction method and analyzed by GC/MS using Method 8250 as detailed in USEPA SW-846 . (Appendix 8).

d) Inorganic constituents will be analyzed by USEPA SW-846, 1982.

e) BHC and HCB will be analyzed by GC/MS Method 8250 as detailed in USEPA SW-846. (Appendix 8).

f) Soils permeability tests will be done on specially collected Shelby tube samples, as per ASTM Method D-2434.68.

B. GROUNDWATER

1) Sample parameters and procedures

a) Samples will be collected from each of the seven monitoring wells.

b) Sample frequency will be once monthly for the first three months and quarterly thereafter for nine months.

2) Sample handling and analysis

a) All samples are to be analyzed for HCB and BHC plus any other materials of Olin manufacture which were detected in soils analyses. Samples for analysis shall not be collected until the contaminants in the soil samples have been identified.

b) All samples except volatile organic samples will be filtered to remove any suspended solids and preserved with proper preservative as per "Sampling and Analytical Procedures for Screening Industrial Effluents for Priority Pollutants", USEPA, 1977. This will be done immediately upon receipt of samples at the contractor's laboratory.

c) After samples are received at the contractor's laboratory, analyses will be done as soon as practical and within the holding times listed in 44 FR 43260.

d) Up to a maximum of five (5) groundwater samples will be analyzed for priority pollutants per "Sampling and Analytical Procedures for Screening Industrial Effluents for Priority Pollutants", USEPA, 1977, or "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater", USEPA, 1982, or "Methods for Chemical Analysis of Water and Waste", USEPA, 1979. The ten (10) non-priority pollutant compounds present in greatest concentration shall also be identified.

e) BHC and HCB will be analyzed by GC/MS in selected ion mode as detailed under soils analysis outline.

C. QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

1) The standard reference for QA/QC procedures during laboratory analysis of samples will be EPA-600 24-79-019, "Handbook for Analytical Quality Control in Water and Wastewater Laboratories", March, 1979.

2) QA/QC for GC/MS laboratory procedures

a) Instrument calibration will be done daily. Precision will be determined by analysis of replicate analysis of same sample.

b) The GC/MS system detection capability will be determined by analysis of standard mixtures, for each type of GC/MS analysis. Standard mixtures will be provided from commercial sources.

c) Additional check is provided by analysis of quality control samples containing four to six compounds after every 10 samples.

d) QA audit samples are analyzed by laboratory, at 5% rate (i.e., one in 20 field samples) for each type of analysis.

e) Non-priority pollutant solvents are utilized in the laboratory for cleaning purposes.

3) QC for trace elements

a) Standards, blanks and duplicates are analyzed for continuous quality control.

b) To check sample digestion, 10% of priority pollutant samples are digested in duplicate. Digestion procedures as per "Sampling and Analysis Procedures for Screening Industrial Effluents for Priority Pollutants". USEPA-April, 1977.

c) After daily instrument calibration, a quality control standard is analyzed to determine recovery.

4) QC practice for inorganic analysis

a) Calibration solutions will be prepared for verification of linear response to standard concentration.

b) Valid analysis of National Bureau of Standards QC sample.

c) Precision verification will be made through duplicate analyses.

d) A standard spike will be run to evaluate recovery and insure absence of matrix interferences.

DLC/GBB/wsr
01/WR9
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Original - 11/11/83

APPENDIX I

Metal Detection

The Fisher TW-5 pipe and cable locator consists of a radio frequency transmitter and receiver. The transmitter outputs a radio signal at 82 kilohertz, frequency modulated at 270 cycles to eliminate outside frequency interference. The signal is transmitted from a loop which yields a perfectly circular field. The receiver unit is mounted on the opposite end of four-foot long handle and, when calibrated using adjustment screws, is parallel to the radio field lines and thus does not detect the signal.

When the radio field lines encounter a metal object, the field lines are distorted and receiver detects the change.

One of the most important features of the unit is that it can be calibrated for various soil conditions (i.e., wet, dry, etc.). As long as the soil conditions are fairly homogeneous, the unit will detect only anomolies such as buried metal.

Shallow groundwater with high totaled dissolved solids may interfere with metal detection if the metal is below the water table. Since this rarely occurs, the interference is not considered a major problem. In fact, in some cases, highly corroded drums have contributed iron or their contents to the groundwater to form locally high TDS waters which can be detected and distinguished from natural waters.

A brine line was installed in the center of the Niagara Mohawk right-of-way in 1969 and 1970 by Buckeye Pipelines Company and Hooker. Hooker owns the brine line easement, purchasing it from Niagara Mohawk. You should note that Niagara Mohawk has indicated that it would be willing to allow Olin free access to the right-of-way wi hout the company having to post bond.

Other than the information set forth herein, we are unaware of any other utility lines having been installed at the site. There are, however, several sewer and water lines along Pine Avenue which may be partially on site property. City and town sewer and water line charts do not include individual connections.

I trust that this information will be helpful to you. Feel free to contact me should any questions arise.

Very truly yours,

Barbara B. Guibord

Barbara B. Guibord
Assistant Counsel

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APPENDIX 5

In-situ Field Permeability Testing

Drawdown/recovery method

Field measurements

- Measure water table level
- Pump standing water out of well casing until dry or until at least one volume has been evacuated, indicating stabilized inflow/outflow conditions.
- Pull pump from well
- Measure and record water table level as well recovers at 15 second intervals of measurement to 1 minute as recovery rate slows.
- Continue recording water table level vs. time for 20-30 minutes, as the water table level approaches its initial level.

Calculations

- Plot water table level (linear scale) vs. time (log scale).
- For part of the drawdown curve conforming to a straight line, measure the drawdown (DS) over one log cycle.
- Calculate aquifer Transmissivity (T) by $T = \frac{264\ Q}{DS}$

  Where Q is the pump rate during the field measurements.
- Aquifer permeability = T - m, the saturated aquifer thickness.

APPENDIX 6

Benzene
Chlorobenzene
Dichlorobenzene
Trichlorobenzene
Tetrachlorobenzene
Pentachlorobenzene
Hexachlorobenzene
Pentachloronitrobenzene
Tetrachloroethylene
Hexachlorocyclohexane - α-isomer
Hexachlorocyclohexane - β-isomer BHC'S
Hexachlorocyclohexane - γ-isomer
Hexachlorocyclohexane - δ-isomer
Heptachlorocyclohexane
Phenylmethylether (anisole)
Trichloroanisole
Chlorinated Biphenyls
Phenol
Dichlorophenols
Trichlorophenols
Formaldehyde
Mercury

78/WR8
1/07/85

APPENDIX 7

METHOD 8240

GC/MS METHOD FOR VOLATILE ORGANICS

1.0 Scope and Application

1.1 Method 8240 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including groundwater, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.2 The detection limit of Method 8240 for an individual compound is approximately 1 µg/g (wet weight) in waste samples. For samples containing more than 1 mg/g of total volatile material, the detection limit is proportionately higher.

1.3 Method 8240 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by or under the supervision of analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 Summary of Method

2.1 The volatile compounds are introduced to the gas chromatograph by direct injection, the Headspace Method (Method 5020), or the Purge-and-Trap Method (Method 5030). Method 5030 should be used for groundwater analysis. The components are separated via the gas chromatograph and detected using a mass spectrometer which is used to provide both qualitative and quantitative information. The chromatographic conditions as well as typical mass spectrometer operating parameters are given.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample can be dispersed in methanol or polyethylene glycol (PEG) to dissolve the volatile organic constituents. A portion of the methanolic or PEG solution is combined with water in a specially designed purging chamber. An inert gas is then bubbled through the solution at ambient temperature and the volatile comnponents are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

2.3 An aliquot of each sample must be spiked with an appropriate standard to determine percent recovery and detection limits for that sample.

2.4 Table 1 lists detection limits that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample would be significantly higher.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min) Column 1[a]	Method detection limit (µg/l)
Chloromethane	2.3	ND
Bromomethane	3.1	ND
Vinyl chloride	3.8	ND
Chloroethane	4.6	ND
Methylene chloride	6.4	2.8
Trichlorofluoromethane	8.3	ND
1,1-Dichloroethene	9.0	2.8
1,1-Dichloroethane	10.1	4.7
trans-1,2-Dichloroethene	10.8	1.6
Chloroform	11.4	1.6
1,2-Dichloroethane	12.1	2.8
1,1,1-Trichloroethane	13.4	3.8
Carbon tetrachloride	13.7	2.8
Bromodichloromethane	14.3	2.2
1,2-Dichloropropane	15.7	6.0
trans-1,3-Dichloropropene	15.9	5.0
Trichloroethene	16.5	1.9
Benzene	17.0	4.4
Dibromochloromethane	17.1	3.1
1,1,2-Trichloroethane	17.2	5.0
cis-1,3-Dichloropropene	17.2	ND
2-Chloroethylvinyl ether	18.6	ND
Bromoform	19.8	4.7
1,1,2,2-Tetrachloroethane	22.1	6.9
Tetrachloroethene	22.2	4.1
Toluene	23.5	6.0
Chlorobenzene	24.6	6.0
Ethyl benzene	26.4	7.2
1,3-Dichlorobenzene	33.9	ND
1,2-Dichlorobenzene	35.0	ND
1,4-Dichlorobenzene	35.4	ND

ND = not determined.

[a]Column conditions: Carbopack B (60/80 mesh) coated with 1% SP-1000 packed in a 6-ft by 2-mm I.D. glass column with helium carrier gas at a flow rate of 30 ml/min. Column temperature is isothermal at 45° C for 3 min, then programmed at 8° C per minute to 220° and held for 15 min.

3.0 Interferences

3.1 Interferences coextracted from the samples will vary considerably from source to source, depending upon the particular waste or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences under the conditions of the analysis by running method blanks. Method blanks are run by analyzing organic-free water in the normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride) through the septum seal into the sample during shipment and storage. A field blank prepared from organic-free water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross contamination can occur whenever high-level and low-level samples are sequentially analyzed. To reduce cross contamination, the purging device and sample syringe should be rinsed out twice, between samples, with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high organohalide levels, it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105° C oven between analyses.

3.4 Low molecular weight impurities in PEG can be volatilized during the purging procedure. Thus, the PEG employed in this method must be purified before use as described in Section 5.2.

4.0 Apparatus and Materials

4.1 Sampling equipment

4.1.1 Vial: 25-ml capacity or larger, equipped with a screw cap (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry for 1 hr at 105° C before use.

4.1.2 Septum: Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water and dry at 105° C for 1 hr before use.

4.2 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the purging chamber, trap, and the desorber. Several complete devices are now commercially available.

4.2.1 The purging chamber must be designed to accept 5-ml or 25-ml samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 ml. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging chamber, illustrated in Figure 1, meets these design criteria.

4.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 2.5 mm. The trap must be packed to contain the following minimum lengths-of-adsorbents: 1.0 cm of methyl-silicone-coated packing (Section 5.3.2), 15 cm of 2,6-diphenylene oxide polymer (Section 5.3.1), and 8 cm of silica gel (Section 5.3.3). The minimum specifications for the trap are illustrated in Figure 2.

4.2.3 The desorber must be capable of rapidly heating the trap to 180° C within 30 sec. The polymer section of the trap should not be heated higher than 180° C and the remaining sections should not exceed 220° C. The desorber design, illustrated in Figure 2, meets these criteria.

4.2.4 The purge-and-trap device may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3 and 4.

4.3 Gas chromatograph/mass spectrometer system

4.3.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.3.2 Column: 2-m x 2-mm I.D. stainless steel or glass, packed with 1% SP-1000 on 60/80 mesh Carbopack B or equivalent.

4.3.3 Mass spectrometer: Capable of scanning from 40 to 250 amu every 3 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet or introduced in the purge-and-trap mode.

4.3.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Section 9) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS.

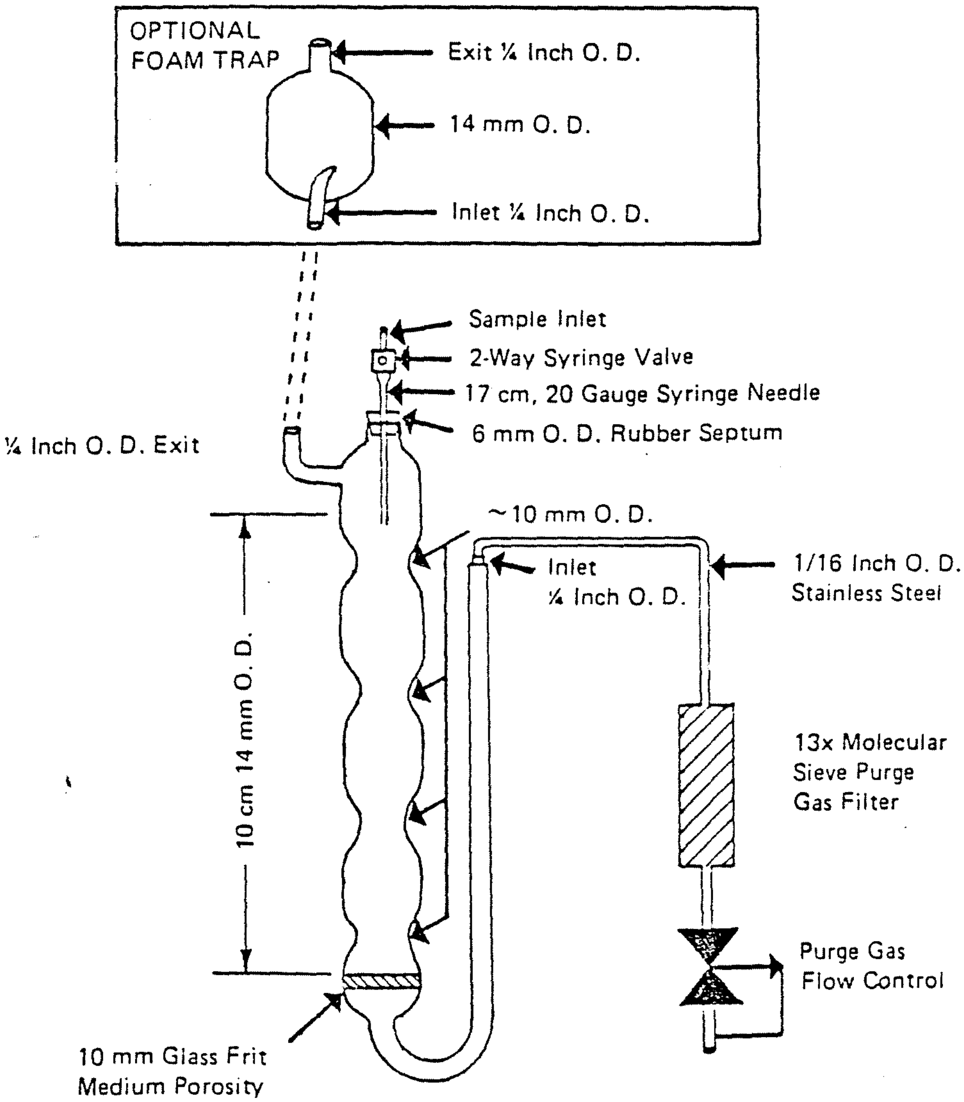

Figure 1. Purging chamber.

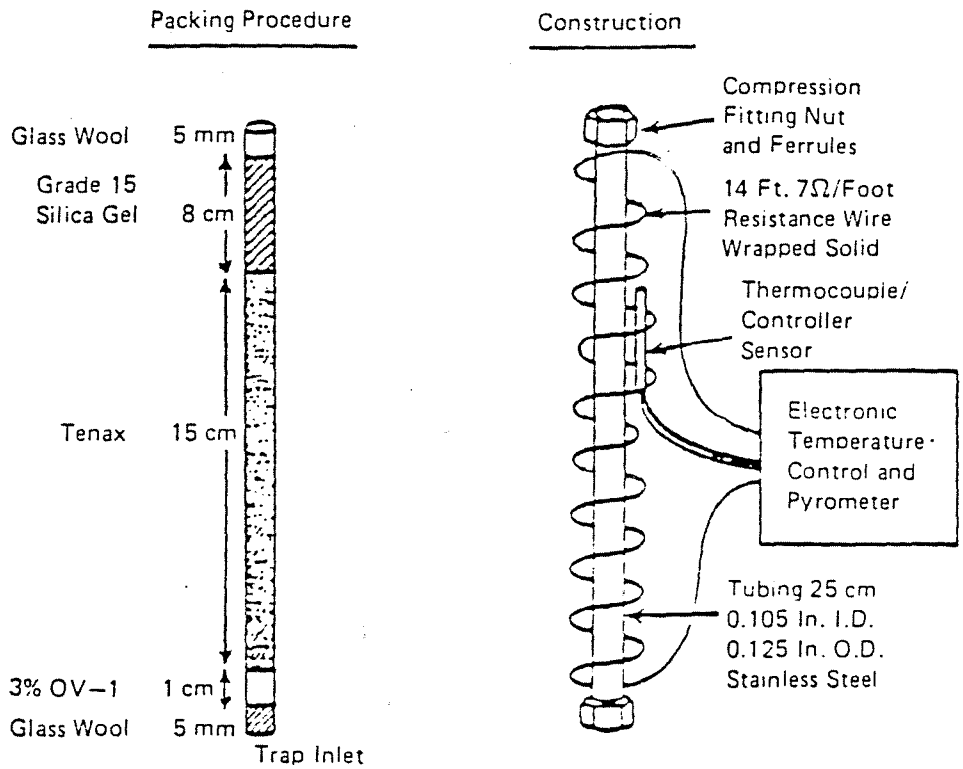

Figure 2. Trap packings and construction to include desorb capability.

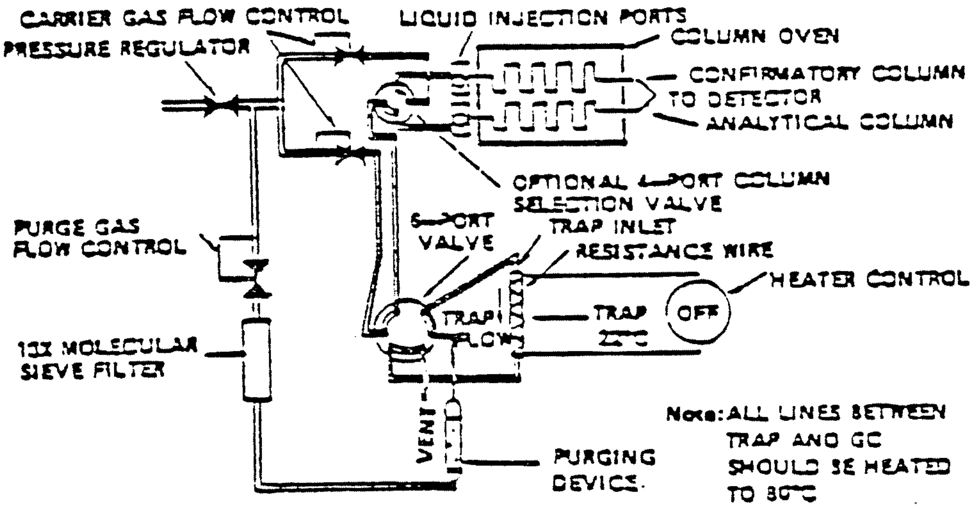

FIGURE 3. Schematic of purge and trap device — purge mode

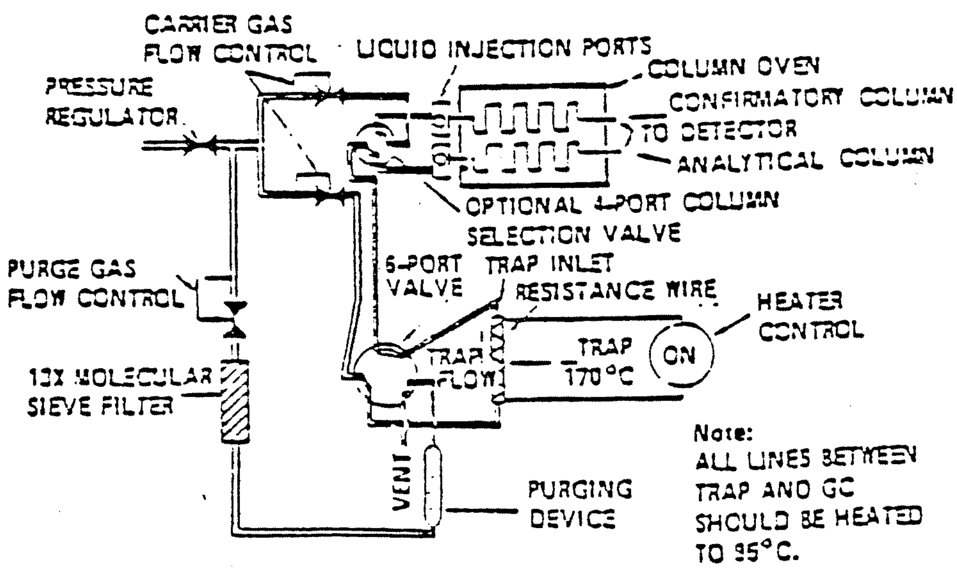

Figure 4. Schematic of purge and trap device - desorb mode

4.3.5 Data system: A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Hardware and software must be available to transform the data into a compatible format. These generally consist of a 9-inch, 800-bpi tape drive and the associated software.

4.4 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. The transfer must be accomplished rapidly to avoid loss of volatile components during the transfer step. Liquids may be transferred using a hypodermic syringe with a wide-bore needle or no needle attached. Samples should be introduced into the syringe by (1) removing the plunger from the syringe, (2) pouring the sample into the barrel, and (3) replacing the barrel and inverting the syringe to remove any air trapped in the syringe. Do not draw the sample up into the syringe. Solids may be transferred using a conventional laboratory spatula, spoon, or coring device. A coring device that is suitable for handling some samples can be made by using a glass tubing saw to cut away the closed end of the barrel of a glass hypodermic syringe.

TABLE 2. BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion abundance criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 100% of mass 174
177	5 to 9% of mass 176

4.5 Syringes: 5-ml and 25-ml glass hypodermic, equipped with 20-gauge needle, at least 15 cm in length.

4.6 Micro syringes: 10-µl, 25-µl, 100-µl, 250-µl, and 1000-µl. These syringes should be equipped with 20-gauge needles having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device (see Figure 1). The needle length required will depend upon the dimensions of the purging device employed.

4.7 Centrifuge tubes: 50-ml round-bottom glass centrifuge tubes with Teflon-lined screw caps. The tubes must be marked before use to show an approximate 20-ml graduation.

4.8 Centrifuge: Capable of accommodating 50-ml glass tubes.

4.9 Syringe valve: 2-way, with Luer ends (2 each) (Hamilton #86725 valve equipped with one Hamilton #35033 Luer fitting, or equivalent).

4.10 Syringe: 5-ml, gas-tight with shut-off valve.

4.11 Bottle: 15-ml, screw-cap, Teflon cap liner.

4.12 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.13 Rotary evaporator: equipped with Teflon-coated seals (Buchi Rotavapor R-110, or equivalent).

4.14 Vacuum pump: mechanical, two-stage.

5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 500 g of activated carbon (Calgon Corp., Filtrasorb-300, or equivalent).

5.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.1.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

5.1.4 Reagent water may also be purchased under the name "HPLC water" from several manufacturers (Burdick and Jackson, Baker and Waters, Inc.).

5.2 Reagent PEG: Reagent PEG is defined as PEG having a nominal average molecular weight of 400, and in which interferents are not observed at the method detection limit for compounds of interest.

5.2.1 Reagent PEG is prepared by purification of commercial PEG having a nominal average molecular weight of 400. The PEG is placed in a round-bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100° C and vacuum is maintained at less than 10 mm Hg for at least 1 hr using a two-stage mechanical pump. The vacuum system is equipped with an all-glass trap, which is maintained in a dry ice/methanol bath.

5.2.2 In order to demonstrate that all interfering volatiles have been removed from the PEG, a reagent water/PEG blank must be analyzed.

5.3 Trap materials

5.3.1 2,6-Diphenylene oxide polymer: 60/80-mesh Tenax, chromatographic grade or equivalent.

5.3.2 Methyl silicone packing: 3 percent OV-1 on 60/80 mesh Chromosorb-W or equivalent.

5.3.3 Silica gel, Davison Chemical (35/60 mesh), grade-15 or equivalent.

5.3.4 Prepared trapping columns may be purchased from several chromatography suppliers.

5.4 Methanol: Distilled-in-glass quality or equivalent.

5.5 Calibration standards; stock solutions (2 mg/ml): Stock solutions of calibration standards may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions of individual compounds in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn by analysts when handling high concentrations of these materials.

5.5.1 Place about 9.8 ml of methanol in a 10-ml ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material as described below.

5.5.2.1 Liquids: Using a 100-µl syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases: To prepare standards for any compounds that boil below 30° C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-ml valved gas-tight syringe with a reference standard to the 5.0-ml mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol.

5.5.3 Reweigh, dilute to volume, stopper, then mix by gently inverting the flask several times. Calculate the concentration in µg/µl per microliter from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.5.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10 to -20° C and protect from light.

5.5.5 Prepare fresh standards weekly for gases or for reactive compounds such as 2-chloroethylvinyl ether. All other standards must be replaced after one month, or sooner if comparison with check standards indicates a problem.

5.6 Calibration standards; secondary dilution solutions: Using stock solutions described in Section 5.5, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the methanol or aqueous PEG calibration solutions prepared as described in Section 6.3.2 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace and should be checked frequently for signs of evaporation, especially just prior to preparing calibration standards from them.

5.7 Surrogate standards: Surrogate standards may be added to samples and calibration solutions to assess the effect of the sample matrix on recovery efficiency. The compounds employed for this purpose are 1,2-dibromotetrafluoroethane, bis(perfluoroisopropyl) ketone, fluorobenzene, and m-bromobenzotrifluoride. Prepare methanolic solutions of the surrogate standards using the procedures described in Sections 5.5 and 5.6. The concentrations prepared and the amount of solution added to each sample should be those required to give an amount of each surrogate in the purging device that is equal to the amount of each internal standard added, assuming a 100% recovery of the surrogate standards.

5.8 Internal standards: In this method, internal standards are employed during analysis of all samples and during all calibration procedures. The analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. However, for general use, D_4-1,2-dichloroethane, D_6-benzene, and D_5-ethylbenzene are recommended as internal standards covering a wide boiling point range.

5.9 4-Bromofluorobenzene (BFB): BFB is added to the internal standard solution or analyzed alone to permit the mass spectrometer tuning for each GC/MS run to be checked.

5.10 Internal standard solution: Using the procedures described in Sections 5.5 and 5.6, prepare a methanolic solution containing each internal standard at a concentration of 12.5 µg/ml.

5.11 Sodium monohydrogen phosphate: 2.0 µ in distilled water.

5.12 n-Nonane and n-dodecane, 98+% purity.

5.13 N-Hexadecane, distilled-in-glass (Burdick and Jackson, or equivalent).

6.0 Sample Collection, Handling, and Preservation

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All samples must be stored in Teflon-lined screw cap vials. Sample containers should be filled as completely as possible so as to minimize headspace or void space. Vials containing liquid sample should be stored in an inverted position.

6.3 All samples must be iced or refrigerated from the time of collection to the time of analysis, and should be protected from light.

7.0 Procedure

7.1 Calibration

7.1.1 Assemble a purge-and-trap device that meets the specifications in Section 4.2 and connect the device to a GC/MS system. Condition the trap overnight at 180° C by backflushing with an inert gas flow of at least 20 ml/min. Prior to use, condition the trap daily for 10 min while backflushing at 180° C.

7.1.2 Operate the gas chromatograph using the conditions described in Section 7.3.5 and operate the mass spectrometer using the conditions described in Section 7.3.2.

7.1.3 Calibration procedure

7.1.3.1 Conduct calibration procedures using a minimum of three concentration levels for each calibration standard. One of the concentration levels should be at a concentration near but above the method detection limit. The remaining two concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.3.2 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. To the purging device, add 5.0 ml of reagent water or reagent water/PEG solution. This solution is prepared by taking 4.0 ml of reagent water or reagent PEG and diluting to 100 ml with reagent water. The reagent water/PEG solution is added to the purging device using a 5-ml glass syringe fitted with a 15-cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of a 20-gauge needle. Next, using a 10-µl or 25-µl micro-syringe equipped with a long needle (see Section 4.6), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (see Section 5.6). Add the aliquot of calibration solution directly to the reagent water or reagent water/PEG solution in the purging device by inserting the needle through the sample inlet. When discharging the contents of the micro-syringe be sure that the end of the syringe needle is well beneath the surface of the reagent water or water/PEG solution. Similarly, add 20 µl of the internal standard solution (see Section 5.10). Close the 2-way syringe valve at the sample inlet.

7.1.3.3 Carry out the purge and analysis procedure as described in Section 7.3.4. Tabulate the area response of the primary characteristic ion against concentration for each compound including the internal standards. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/A_{is} C_s)$$

where:

A_s = Area of the primary characteristic ion for the compound to be measured

A_{is} = Area of the primary characteristic ion of the internal standard

C_{is} = Concentration of the internal standard

C_s = Concentration of the compound to be measured.

The internal standard selected for the calculation of the RF of a compound and subsequent quantification of the compound is generally the internal standard that has a retention time closest to that of the compound. It is assumed that a linear calibration plot will be obtained over the range of concentrations used. If the RF value over the working range is a constant (less than 10% relative standard deviation), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, versus RF.

7.1.3.4 The RF must be verified on each working day. The concentrations selected should be near the midpoint of the working range. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within ±20% of the response factor used for quantification of the sample concentrations.

7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for BFB (see Table 2).

7.2.2 The BFB performance test requires the following instrumental parameters:

Electron Energy:	70 volts (nominal)
Mass Range:	40 to 250 amu
Scan Time:	to give approximately 6 scans per peak but not to exceed 3 sec per scan.

7.2.3 Bleed BFB vapor into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of BFB given in Table 1. A solution containing 20 ng of BFB may be injected onto the gas chromatographic column in order to check the key ion criteria.

7.2.4 The peak intensity of D_6-benzene is used to monitor the mass spectrometer sensitivity. The peak intensity for D_6-benzene observed during each sample analysis must be between 0.7 and 1.4 times the D_6-benzene peak intensity observed during the applicable calibration runs. For example, if the peak intensity of D_6-benzene observed during calibration was 355,000 area counts, then each subsequent sample or blank must give a D_6-benzene peak intensity of between 250,000 and 500,000 area counts. If the D_6-benzene peak intensity is outside the specified range, the sample must be reanalyzed. If the peak intensity is again outside the specified range, the analyst must investigate the cause of the variability in sensitivity and correct the problem.

7.3 Sample extraction and analysis

7.3.1 The analytical procedure involves extracting the non-aqueous sample with methanol or polyethylene glycol (PEG) and analyzing a portion of the extract by a purge-and-trap GC/MS procedure. The amount of the extract to be taken for the GC/MS analysis is based on the estimated total volatile content (TVC) of the sample. The TVC is estimated by extracting the sample with n-hexadecane and analyzing the n-hexadecane extract by gas chromatography.

7.3.2 The estimated TVC is based on the total area response relative to that of n-nonane for all components eluting prior to the retention time of n-dodecane. The response factor for n-nonane and the retention time of n-dodecane are determined by analyzing a 2-µl aliquot of an n-hexadecane solution containing 0.20 mg/ml of n-nonane and n-dodecane.

7.3.2.1 The GC analyses are conducted using a flame ionization detector and a 3-m x 2-mm I.D. glass column packed with 10% OV-101 on 100-200 mesh Chromosorb W-HP. The column temperature is programmed from 80° C to 280° C at 8°/min and held at 280° for 10 min.

7.3.2.2 Determine the area response for n-nonane and divide by 0.2 to obtain the area response factor. Record the retention time of n-dodecane.

7.3.2.3 Add 1.0 g of sample to 20 ml of n-hexadecane and 2 ml of 2.0 M Na_2HPO_4 contained in a 50-ml glass centrifuge tube and cap securely with a Teflon-lined screw cap. Shake the mixture vigorously for one minute. If the sample does not disperse during the shaking process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate phase separation.

7.3.2.4 Analyze a 2-µl aliquot of the n-hexadecane supernatant using the conditions described in Section 7.3.2.1. Determine the total area response of all components eluting prior to the retention time of n-dodecane and subtract the corresponding area of an n-hexadecane blank. Using the area response factor determined for n-nonane in Section 7.3.2.2, calculate the TVC as follows:

$$TVC = \frac{TAR_{sample} - TAR_{blank}}{\text{n-Nonane Area Response Factor}} \times 20$$

where:

TVC = total volatile content of the sample in mg/g

TAR_{sample} = total area response obtained for the sample

TAR_{blank} = total area response obtained for a blank.

7.3.3 The transfer of an aliquot of the sample for extraction with methanol or PEG should be made as quickly as possible to minimize loss of volatiles from the sample.

7.3.3.1 To a 50-ml glass centrifuge tube with Teflon-lined cap, add 40 ml of reagent methanol or PEG. Weigh the capped centrifuge tube and methanol or PEG on an analytical balance.

7.3.3.2 Using an appropriate implement (see Section 4.4), transfer approximately 2 g of sample to the methanol or PEG in the centrifuge tube in such a fashion that the sample is dissolved in or submerged in the methanol or PEG as quickly as possible. Take care not to touch the sample-transfer implement to the methanol or PEG. Recap the centrifuge tube immediately and weigh on an analytical balance to determine an accurate sample weight.

7.3.3.3 Disperse the sample by vigorous agitation for 1 min. The mixture may be agitated manually or with the aid of a vortex-mixer. If the sample does not disperse during this process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained as the sample extract. Centrifuge if necessary to facilitate phase separation.

7.3.3.4 The sample extract may be stored for future analytical needs. If this is desired, transfer the solution to a 10-ml screw cap vial with Teflon cap liner. Store at -10 to -20° C, and protect from light.

7.3.4 Reagent water, internal standard solution, and the sample extract are added to a purging chamber that is connected to the purge-and-trap device and that has been flushed with helium during a 7-min trap reconditioning step (see Section 7.3.4.4). The additions are made using an appropriately sized syringe equipped with a 15-cm 20-gauge needle. Open the syringe valve of the sample inlet (shown in Figure 1) and insert the needle through the valve.

7.3.4.1 Add 5.0 ml of reagent water or aqueous sample to which 20.0 µl of the internal standard solution has been added (see Section 5.10) to the purging chamber. Insert the needle of the syringe well below the surface of the water for the addition of the internal standard solution. If the sample is aqueous go to Section 7.3.5.

7.3.4.2 Add an aliquot of the sample extract from Section 7.3.3.4. The total quantity of volatile components injected should not exceed approximately 10 µg. If the total volatile content (TVC) of the sample as determined in Section 7.3.1.4 is 1.0 mg/g or less, use a 200-µl aliquot of the sample extract. If the TVC is greater than 1.0 mg/g, use an aliquot of the sample extract that contains approximately 10 µg of total volatile components; the volume (in µl) of the aliquot to be taken can be calculated by dividing 200 by the TVC. If the TVC is greater than 20 mg/g, take a 500-µl aliquot of the sample extract and dilute to 10 ml with PEG. In this case calculate the aliquot volume (in µl) of the undiluted extract to be taken by dividing 4,000 by the TVC. If the TVC is less than 1.0 mg/g and greater sensitivity is desired, use a large purging chamber containing 25 ml of reagent water and use a 1.0-ml aliquot of the sample extract.

7.3.4.3 Close the 2-way syringe valve at the sample inlet.

7.3.5 The sample in the purging chamber is purged with helium to transfer the volatile components to the trap. The trap is then heated to desorb the volatile components which are swept by the helium carrier gas onto the GC column for analysis.

7.3.5.1 Adjust the gas (helium) flow rate to 40 ± 3 ml/min. Set the purging device to purge, and purge the sample for 11.0 ± 0.1 min at ambient temperature.

7.3.5.2 At the conclusion of the purge time, adjust the device to the desorb mode, and begin the GC/MS analysis and data acquisition using the following GC operating conditions:

Column: 6-ft x 2-mm I.D. glass column of 1% SP-1000 on Carbo-pack B (60-80 mesh).

Temperature: Isothermal at 45° C for 3 min, then increased at 8° C/min to 220° C, and maintained at 220° C for 15 min.

Concurrently, introduce the trapped materials to the GC column by rapidly heating the trap to 180° C while backflushing the trap with helium at a flow rate of 30 ml/min for 4 min. If this rapid heating requirement cannot be met, the GC column must be used as a secondary trap by cooling it to 30° C or lower during the 4-min desorb step and starting the GC program after the desorb step.

7.3.5.3 Return the purge-and-trap device to the purge mode and continue acquiring GC/MS data.

7.3.5.4 Allow the trap to cool for 8 min. Replace the purging chamber with a clean purging chamber. The purging chamber is cleaned after each use by sequential washing with acetone, methanol, detergent solution and distilled water, and then dried at 105° C.

7.3.5.5 Close the syringe valve on the purging chamber after 15 sec to begin gas flow through the trap. Purge the trap at ambient temperature for 4 min. Recondition the trap by heating it to 180° C. Do not allow the trap temperature to exceed 180° C, since the sorption/desorption is adversely affected when the trap is heated to higher temperatures. After heating the trap for approximately 7 min, turn off the trap heater. When cool, the trap is ready for the next sample.

7.3.6 If the response for any ion exceeds the working range of the system, repeat the analysis using a correspondingly smaller aliquot of the sample extract described in Section 7.3.2.3.

7.4 Qualitative identification

7.4.1 Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

7.4.1.1 The characteristic ions of each compound of interest must maximize in the same or within one scan of each other.

7.4.1.2 The retention time must fall within ±30 sec of the retention time of the authentic compound.

7.4.1.3 The relative peak heights of the characteristic ions in the EICP's must fall within ±20% of the relative intensities of these ions in a reference mass spectrum. Reference spectra may be generated from the standards analyzed by the analyst or from a reference library. All reference spectra generated from standards must be obtained from an appropriately tuned mass spectrometer.

7.5 Quantitative determination

7.5.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion, as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used. Generally, the base peak of the mass spectrum is used.

8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of the data that are generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.1.3 Before processing any samples, the analyst should daily demonstrate, through the analysis of an organic-free water method blank, that the entire analytical system is interference-free. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations using a representative sample as a check sample.

8.2.1 Analyze four aliquots of the unspiked check sample according to the method in Section 7.3.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methanol at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples by adding the spiking solution to the PEG used for the extraction. Analyze the spiked aliquots according to the method in Section 7.3.

8.2.4 Calculate the average percent recovery, R, and the standard deviation of the percent recovery, s, for all compounds and surrogate standards. Background corrections must be made before R and s calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery, s/R x 100, must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.4:

Upper Control Limit (UCL) = R + 3s
Lower Control Limit (LCL) = R - 3s

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the R and s values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standards to monitor spike recoveries. The spiking level used should be that which will give an amount in the purge apparatus that is equal to the amount of the internal standard assuming a 100% recovery of the surrogate standards. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as being outside of control limits. The laboratory must monitor the frequency of data so qualified to ensure that it remains at or below 5%. Four surrogate standards, namely 1,2-dibromodifluoroethane, bis(perfluoro-isopropyl) ether, fluorobenzene, and m-bromobenzotrifluoride, are recommended for general use to monitor recovery of volatile compounds varying in volatility and polarity.

8.5 Each day, the analyst must demonstrate through the analysis of a process blank that all glassware and reagent interferences are under control.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

8.7 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.8 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.9 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 3 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 3.

TABLE 3. ACCURACY AND PRECISION FOR PURGEABLE ORGANICS

Parameter	Reagent Water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
Benzene	99	9	98	10
Bromodichloromethane	102	12	103	10
Bromoform	104	14	105	16
Bromomethane	100	20	88	23
Carbon tetrachloride	102	16	104	15
Chlorobenzene	100	7	102	9
Chloroethane	97	22	103	31
2-Chloroethyl vinyl ether	101	13	95	17
Chloroform	101	10	101	12
Chloromethane	99	19	99	24
Dibromochloromethane	103	11	104	14
1,1-Dichloroethane	101	10	104	15
1,2-Dichloroethane	100	8	102	10
1,1-Dichloroethene	102	17	99	15
trans-1,2-Dichloroethene	99	12	101	10
1,2-Dichloropropane	102	8	103	12
cis-1,3-Dichloropropene	105	15	102	19
trans-1,3-Dichloropropene	104	11	100	18
Ethyl benzene	100	8	103	10
Methylene chloride	96	16	89	28
1,1,2,2-Tetrachloroethane	102	9	104	14
Tetrachloroethene	101	9	100	11
Toluene	101	9	98	14
1,1,1-Trichloroethane	101	11	102	16
1,1,2-Trichloroethane	101	10	104	15
Trichloroethene	101	9	100	12
Trichlorofluoromethane	103	11	107	19
Vinyl chloride	100	13	98	25

Samples were spiked between 10 and 1000 µg/l.

METHOD 8250

GC/MS METHOD FOR SEMIVOLATILE ORGANICS: PACKED COLUMN TECHNIQUE

1.0 Scope and Application

1.1 Method 8250 is used to determine the concentration of semivolatile organic compounds (see Tables 1 and 2) in a variety of solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including groundwater, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 Method 8250 can be used to quantify most neutral, acidic, and basic organic compunds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic column. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

1.4 The detection limit of Method 8250 for determining an individual compound is approximately 1 µg/g (wet weight) in waste samples. For samples that contain more than 1 mg/g of total solvent extractable material, the detection limit is proportionately higher.

1.5 Method 8250 is based upon a solvent extraction, gas chromatographic/ mass spectrometric (GC/MS) procedure.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of Method

2.1 Prior to using this method, the waste samples should be prepared for chromatography (if necessary) using the appropriate sample preparation method - i.e., separatory funnel liquid-liquid extraction (Method 3510), acid base extraction (Method 3530), sonication (Method 3550), or soxhlet extraction (Method 3540). For groundwater samples Method 3530 should be used. If emulsions are a problem, continuous extraction techniques should be used. This method describes chromatographic conditions which allow for the separation of the compounds in the extract.

TABLE 1. CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC IONS FOR BASE/NEUTRAL EXTRACTABLES

Parameter	Retention time (min)	Method detection limit (µg/l)	Characteristic ions: Electron impact, Primary	Electron impact, Secondary		Chemical ionization (methane)		
1,3-Dichlorobenzene	7.4	1.9	146	148	113	146	148	150
1,4-Dichlorobenzene	7.8	4.4	146	148	113	146	148	150
Hexachloroethane	8.4	1.6	117	201	199	199	201	203
Bis(2-chloroethyl) ether	8.4	5.7	93	63	95	63	107	109
1,2-Dichlorobenzene	8.4	1.9	146	148	113	146	148	150
Bis(2-chloroisopropyl) ether	9.3	5.7	45	77	79	77	135	137
N-Nitrosodi-n-propyl amine			130	42	101			
Nitrobenzene	11.1	1.9	77	123	65	124	152	164
Hexachlorobutadiene	11.4	0.9	225	223	227	223	225	227
1,2,4-Trichlorobenzene	11.6	1.9	180	182	145	181	183	209
Isophorone	11.9	2.2	82	95	138	139	167	178
Naphthalene	12.1	1.6	128	129	127	129	157	169
Bis(2-chloroethoxy) methane	12.2	5.3	93	95	123	65	107	137
Hexachlorocyclopentadiene	13.9		237	235	272	235	237	239
2-Chloronaphthalene	15.9	1.9	162	164	127	163	191	203
Acenaphthylene	17.4	3.5	152	151	153	152	153	181
Acenaphthene	17.8	1.9	154	153	152	154	155	183
Dimethyl phthalate	18.3	1.6	163	194	164	151	163	164
2,6-Dinitrotoluene	18.7	1.9	165	89	121	183	211	223
Fluorene	19.5	1.9	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	19.5	4.2	204	206	141			
2,4-Dinitrotoluene	19.8	5.7	165	63	182	183	211	223
Diethylphthalate	20.1	22	149	177	150	177	223	251
N-Nitrosodiphenylamine	20.5	1.9	169	168	167	169	170	198
Hexachlorobenzene	21.0	1.9	284	142	249	284	286	288
α-BHC	21.1		183	181	109			
4-Bromophenyl phenyl ether	21.2	1.9	248	250	141	249	251	277
γ-BHC	22.4		183	181	109			

TABLE 1. (CONT.)

Parameter	Retention time (min)	Method detection limit (µg/l)	Characteristic ions: Electron impact, Primary	Electron impact, Secondary		Chemical ionization (methane)		
Phenanthrene	22.8	5.4	178	179	176	178	179	207
Anthracene	22.8	1.9	178	179	176	178	179	207
β-BHC	23.4	4.2	181	183	109			
Heptachlor	23.4	1.9	100	272	274			
δ-BHC	23.7	3.1	183	109	181			
Aldrin	24.0	1.9	66	263	220			
Dibutyl phthalate	24.7	2.5	149	150	104	149	205	279
Heptachlor epoxide	25.6	2.2	353	355	351			
Endosulfan I	26.4	--	237	339	341			
Fluoranthene	26.5	2.2	202	101	100	203	231	243
Dieldrin	27.2	2.5	79	263	279			
4,4'-DDE	27.2	5.6	246	248	176			
Pyrene	27.3	1.9	202	101	100	203	231	243
Endrin	27.9	--	81	263	82			
Endosulfan II	28.6	--	237	339	341			
4,4'-DDD	28.6	2.8	235	237	165			
Benzidine	28.8	44	184	92	185	185	213	225
4,4'-DDT	29.3	4.7	235	237	165			
Endosulfan sulfate	29.8	5.6	272	387	422			
Endrin aldehyde	--	--	67	345	250			
Butyl benzyl phthalate	29.9	2.5	149	91	206	149	299	327
Bis(2-ethylhexyl) phthalate	30.6	2.5	149	167	279	149		
Chrysene	31.5	2.5	228	226	229	228	229	257
Benzo(a)anthracene	31.5	7.8	228	229	226	228	229	257
3,3'-Dichlorobenzidine	32.2	16.5	252	254	126			
Di-n-octyl phthalate	32.5	2.5	149					
Benzo(b)fluoranthene	34.9	4.8	252	253	125	252	253	281
Benzo(k)fluoranthene	34.9	2.5	252	253	125	252	253	281
Benzo(a)pyrene	36.4	2.5	252	253	125	252	253	281

TABLE 1. (CONT.)

Parameter	Retention time (min)	Method detection limit (µg/l)	Characteristic ions: Electron impact Primary	Electron impact Secondary		Chemical ionization (methane)		
Indeno(1,2,3-c,d)pyrene	42.7	3.7	276	138	277	276	277	305
Dibenzo(a,h)anthracene	43.2	2.5	278	139	279	278	279	307
Benzo(ghi)perylene	45.1	4.1	276	138	277	276	277	305
N-Nitrosodimethyl amine	--	--	42	74	44			
Chlordane[a]	19 to 30	--	373	375	377			
Toxaphene[a]	25 to 34	--	159	231	233			
PCB 1016[a]	18 to 30	--	224	260	294			
PCB 1221[a]	15 to 30	30	190	224	260			
PCB 1232[a]	15 to 32	--	190	224	260			
PCB 1242[a]	15 to 32	--	224	260	294			
PCB 1248[a]	12 to 34	--	294	330	362			
PCB 1254[a]	22 to 34	36	294	330	362			
PCB 1260[a]	23 to 32	--	330	362	394			

[a]These compounds are mixtures of various isomers (See Figures 2 to 12).

Gas chromatographic conditions: Glass column 1.8 m long x 2 mm I.D. packed with Supelcoport (100/120) coated with 3% SP-2250. Carrier gas: helium at a flow rate of 30 ml/min. Temperature: Isothermal at 50° C for 4 min, then 8° per min to 270° C. Hold at 270° C for 30 min.

TABLE 2. CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC IONS FOR ACID EXTRACTABLES

Parameter	Retention time (min)	Method detection limit (µg/l)	Characteristic ions: Electron impact, Primary	Electron impact, Secondary		Chemical ionization (methane)		
2-Chlorophenol	5.9	3.3	128	64	130	129	131	157
2-Nitrophenol	6.5	3.6	139	65	109	140	168	122
Phenol	8.0	1.5	94	65	66	95	123	135
2,4-Dimethylphenol	9.4	2.7	122	107	121	123	151	163
2,4-Dichlorophenol	9.8	2.7	162	164	98	163	165	167
2,4,6-Trichlorophenol	11.8	2.7	196	198	200	197	199	201
4-Chloro-3-methylphenol	13.2	3.0	142	107	144	143	171	183
2,4-Dinotrophenol	15.9	42	184	63	154	185	213	225
2-Methyl-4,6-dinitrophenol	16.2	24	198	182	77	199	227	239
Pentachlorophenol	17.5	3.6	266	264	268	267	265	269
4-Nitrophenol	20.3	2.4	65	139	109	140	168	122

Chromatographic conditions: Glass column 1.8 m long x 2 mm I.D. packed with Supelcoport (100/120) coated with 1% SP-1240 DA. Carrier gas: helium at a flow rate of 30 ml/min. Column temperature, isothermal at 70° C for 2 min, then 8° per min to 200° C.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or waste being sampled.

3.2.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Heating in a muffle furnace at 450° C for 5 to 15 hr is recommended whenever feasible. Alternatively, detergent washes, water rinses, acetone rinses, and oven drying may be used. Cleaned glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems.

4.0 Apparatus

4.1 Sampling equipment: Glass screw-cap vials or jars of at least 100-ml capacity. Screw caps must be Teflon lined.

4.2 Glassware

4.2.1 Beaker: 400-ml.

4.2.2 Centrifuge tubes: approximately 200-ml capacity, glass with screw cap (Corning #1261 or equivalent). Screw caps must be fitted with Teflon liners.

4.2.3 Concentrator tube, Kuderna-Danish: 25-ml, graduated (Kontes K 570050-2526 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.2.4 Evaporative flask: Kuderna-Danish 250-ml (Kontes K-570001-0250 or equivalent). Attach to concentrator tube with springs.

4.2.5 Snyder column, Kuderna-Danish: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.6 Snyder column, Kuderna-Danish: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3 Filter assembly

4.3.1 Syringe: 10-ml gas-tight with Teflon Luerlock (Hamilton 1010TLL or equivalent).

4.3.2 Filter holder: 13-mm Swinny (Millipore XX30-012 or equivalent)

4.3.3 Prefilters: glass fiber (Millipore AP-20-010 or equivalent).

4.3.4 Membrane filter: 0.2-μm Teflon (Millipore FGLP-013 or equivalent)

4.4 Micro syringe: 100-μl (Hamilton #84858 or equivalent).

4.5 Weighing pans, micro: approximately 1-cm diameter aluminum foil. Purchase or fabricate from aluminum foil.

4.6 Boiling chips: Approximately 10-40 mesh carborundum (A.H. Thomas #1590-D30 or equivalent). Heat to 450° C for 5-10 hr or extract with methylene chloride.

4.7 Water bath: Heated, capable of temperature control (±2° C). The bath should be used in a hood.

4.8 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.9 Microbalance: Capable of accurately weighing to 0.001 mg (Mettler model ME-30 or equivalent).

4.10 Homogenizer, high speed: Brinkmann Polytron model PT 10ST with Teflon bearings, or equivalent.

4.11 Centrifuge: Capable of accommodating 200-ml glass centrifuge tubes.

4.12 pH Meter and electrodes: Capable of accurately measuring pH to ±0.1 pH unit.

4.13 Spatula: Having a metal blade 1-2 cm in width.

4.14 Heat lamp: 250-watt reflector-type bulb (GE #250R-40/4 or equivalent) in a heat-resistant fixture whose height above the sample may be conveniently adjusted.

4.15 Gas chromatograph/mass spectrometer data system

4.15.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.15.2 Column for base-neutral compounds: 2-m x 2-mm I.D. stainless steel or glass, packed with 3% SP-2250-DB on 100/120 mesh Supelcoport B or equivalent.

4.15.3 Column for acidic compounds: 2-m x 2-mm I.D. glass packed with 1% SP 1240-DA on 100/120 mesh Supelcoport.

4.15.4 Mass spectrometer: Capable of scanning from 35 to 450 amu every 3 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 3 when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

TABLE 3. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a]

Mass	Ion abundance criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

[a]J.W. Eichelberger, L.E. Harris, and W.L. Budde. 1975. Reference compound to calibrate ion abundance measurement in gas chromatography-mass spectrometry. Analytical Chemistry 47:995.

4.15.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Sections 7.2.1-7.2.4) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS.

4.15.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

4.16 Gel permeation chromatography system

4.16.1 Chromatographic column: 600-mm x 25-mm I.D. glass column fitted for upward flow operation.

4.16.2 Bio-beads S-X8: 80 g per column.

4.16.3 Pump: Capable of constant flow of 0.1 to 5 ml/min at up to 100 psi.

4.16.4 Injector: With 5-ml loop.

4.16.5 Ultraviolet detector: 254 mm.

4.16.6 Strip chart recorder.

5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each compound of interest.

5.2 Potassium phosphate, tribasic (K_3PO_4): Granular (ACS).

5.3 Phosphoric acid (H_3PO_4): 85% aqueous solution (ACS).

5.4 Sodium sulfate, anhydrous (Na_2SO_4): Powder (ACS).

5.5 Methylene chloride: Distilled-in-glass quality (Burdick and Jackson, or equivalent).

5.6 D_{10}-Phenanthrene.

5.7 Decafluorotriphenylphosphine (DFTPP).

5.8 Retention time standards: D_3-Phenol, D_8-naphthalene, D_{10}-Phenanthrene, D_{12}-chrysene, and D_{12}-benzo(a)pyrene. D_{12}-perylene may be used in place of D_{12}-benzo(a)pyrene.

5.9 Column performance standards: D_3-phenol, D_5-aniline, D_5-nitrobenzene, and D_3-2,4-dinitrophenol.

5.10 Surrogate standards: Decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol.

5.11 GPC calibration solution: Methylene chloride containing 100 mg corn oil, 20 mg di-n-octyl phthalate, 3 mg coronene, and 2 mg sulfur per 100 ml.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers having Teflon-lined screw caps. Sampling equipment must be free of oil and other potential sources of contamination.

6.2 The samples must be iced or refrigerated at 4° C from the time of collection until extraction.

6.3 All samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

7.0 Procedure

7.1 Calibration

7.1.1 An internal standard calibration procedure is used. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that measurement of the internal standard is not affected by method or matrix interferences. D_{10}-phenanthrene is recommended for this purpose for general use. Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next most intense ion as the secondary ion. The internal standard is added to all calibration standards and all sample extracts analyzed by GC/MS. Retention time standards, column performance standards, and a mass spectrometer tuning standard are included in the internal standard solution used.

7.1.1.1 A set of five or more retention time standards is selected that will permit all components of interest in a chromatogram to have retention times of 0.85 to 1.20 relative to at least one of the retention time standards. The retention time standards should be similar in analytical behavior to the compounds of interest and their measurement should not be affected by method or matrix interferences. The following retention time standards are recommended for general use: D_3-phenol, D_8-naphthalene, D_{12}-chrysene, and D_{12}-benzo(a)pyrene. D_{15}-perylene may be substituted for D_{12}-benzo(a)pyrene. D_{10}-phenanthrene serves as a retention time standard as well as an internal standard.

7.1.1.2 Representative acidic, basic, and polar netural compounds are added with the internal standard to assess the column performance of the GC/MS system. The measurement of the column performance standards should not be affected by method or matrix interferences. The following column performance standards are recommended for general use: D_5-phenol, D_5-aniline, D_5-nitrobenzene, and D_3-2,4-dinitrophenol. These compounds can also serve as retention time standards if appropriate and the retention time standards recommended in Section 7.1.1.1 can serve as column performance standards if appropriate.

7.1.1.3 Decafluorotriphenylphosphine (DFTPP) is added to the internal standard solution to permit the mass spectrometer tuning for each GC/MS run to be checked.

7.1.1.4 Prepare the internal standard solution by dissolving, in 50.0 ml of methylene chloride, 10.0 mg of each standard compound specified in Sections 7.1.1.1, 7.1.1.2, and 7.1.1.3. The resulting solution will contain each standard at a concentration of 200 µg/ml.

7.1.2 Prepare calibration standards at a minimum of three concentration levels for each compound of interest. Each ml of each calibration standard or standard mixture should be mixed with 250 µl of the internal standard solution. One of the calibration standards should be at a concentration near, but above, the method detection limit, 1 to 10 µg/ml, and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.3 Analyze 1 µl of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including standard compound. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standards.

C_{is} = Concentration of the internal standard in µg/l.

C_s = Concentration of the compound to be measured in µg/l.

if the RF value over the working range is constant (less than 20% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, against RF.

7.1.4 The RF must be verified on each working day by the measurement of two or more calibration standards, including one at the beginning of the day and one at the end of the day. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within $\pm$20% of the response factor used for quantification of the sample concentrations.

7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for DFTPP.

7.2.2 The DFTPP performance test requires the following instrumental parameters:

Electron energy: 70 volts (nominal)

Mass Range: 40 to 450 amu

Scan Time: 1 sec per scan

7.2.3 Inject a solution containing 50 µg/ml of DFTPP into the GC/MS system or bleed DFTPP vapor directly into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of DFTPP given in Table 1.

7.2.4 DFTPP is included in the internal standard solution added to all samples and calibration solutions. If any key ion abundance observed for DFTPP during the analysis of a sample differs by more than 10% from that observed during the analysis of the calibration solution, then the analysis in question is considered invalid. The instrument must be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

7.3 Sample extraction

7.3.1 The extraction procedure involves homogenization of the sample with methylene chloride, neutralization to pH 7, and the addition of anhydrous sodium sulfate to remove the water. The amount of acid or base required for the neutralization is determined by titration of the sample. Aqueous samples are extracted using Method 3510 while organic liquids may be analyzed neat or diluted with CH_2 and analyzed. Solids and semisolids are extracted by Method 3540 and 3550 or by the extraction described in Steps 7.3.1 through 7.4.3.

7.3.1.1 Thoroughly mix the sample to enable a representative sample to be obtained. Weight 3.0 g (wet weight) of sample into a 400-ml beaker. Add 75 ml methylene chloride and 150 ml water.

7.3.1.2 Homogenize the mixture for a total of 1 min using a high-speed homogenizer. Use a metal spatula to dislodge any material that adheres to the beaker or to the homogenizer before or during the homogenization to ensure thorough dispersion of the sample.

7.3.1.3 Adjust the pH of the mixture to 7.0 $\pm$ 0.2 by titration with 0.4 M H_3PO_4 or 0.4 M K_3PO_4 using a pH meter to measure the pH. Record the volume of acid or base required.

7.3.2 The extraction with methylene chloride is performed using a fresh portion of the sample. Weigh 3.0 g (wet weight) of sample into a 200-ml centrifuge tube. Spike the sample with surrogate standards as described in Section 8.4. Add 150 ml of methylene chloride followed by 1.0 ml of 4 M phosphate buffer pH 7.0, and an amount of 4 M H_3PO_4 or 4 M K_3PO_4 equal to one tenth of the pH 7 acid or base volume requirement determined in Section 7.3.1.3. For example, if the acid requirement in Section 7.3.1.3 was 2.0 ml of 0.4 M H_3PO_4, the amount of 4 M H_3PO_4 needed would be 0.2 ml.

7.3.3 Homogenize the mixture for a total of 30 sec using a high-speed homogenizer at full speed. Cool the mixture in an ice bath or cold water bath, if necessary, to maintain a temperature of 20-30° C. Use a metal spatula to help dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization to obtain as thorough a dispersion of the sample as possible. Some samples, especially those that contain much water, may not disperse well in this step but will disperse after sodium sulfate is added. Add an amount of anhydrous sodium sulfate powder equal to 15.0 g plus 3.0 g per ml of the 4 M H_3PO_4 or 4 M K_3PO_4 added in Section 7.3.2. Homogenize the mixture again for a total of 30 sec using a high-speed homogenizer at full speed. Use a metal spatula to dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization to ensure thorough dispersion. (NOTE: This step may cause rapid deterioration of the Teflon bearing in the homogenizer. The bearing must be replaced whenever the rotor shaft becomes loose to prevent damage to stainless steel parts.) Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate the phase separation. Filter the supernatant required for Sections 7.3.4, 7.3.5, and 7.3.7 (at least 2 ml) through a 0.2-μm Teflon filter.

7.3.4 Estimate the total solvent extractable content (TSEC) of the sample by determining the residue weight of an aliquot of the supernatant from Section 7.3.3. Transfer 0.1 ml of the supernatant to a tared aluminum weighing dish, place the weighing dish under a heat lamp at a distance of 8 cm from the lamp for 1 min to allow the solvent to evaporate, and weigh on a microbalance. If the residue weight of the 0.1-ml aliquot is less than 0.05 mg, concentrate 25 ml of the supernatant to 1.0 ml and obtain a residue weight on 0.1 ml of the concentrate. For the concentration step, use a 25-ml evaporator tube fitted with a micro Snyder column; add two boiling chips and heat in a water bath at 60-65° C. Calculate the TSEC as milligrams of residue per gram of sample using Equation 1 if concentration was not required or Equation 2 if concentration was required.

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of supernatant}}{0.002} \qquad \text{(Eq. 1)}$$

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of conc. supernatant}}{0.05} \qquad \text{(Eq. 2)}$$

7.3.5 If the TSEC of the sample (as determined in Section 7.3) is less than 50 mg/g, concentrate an aliquot of the supernatant that contains a total of only 10 to 20 mg of residual material. For example, if the TSEC is 44 mg/g, use a 20-ml aliquot of the supernatant, which will contain 17.6 mg of residual material, or if the TSEC is 16 mg/g, use a 50-ml aliquot of the supernatant, which will contain 16.0 mg of residual material. If the TSEC is less than 10 mg/g, use 100 ml of the supernatant. Perform the concentration by transferring the aliquot of the supernatant to a K-D flask fitted into a 25-ml concentrator tube. Add two boiling chips, attach a three-ball macro Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65° C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation, the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an apparent volume of 5 to 6 ml, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 min while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with the methylene chloride to bring the volume to 10.0 ml. Mix the contents of the concentrator tube by inserting a stopper and inverting several times.

7.3.6 Analyze the concentrate from Section 7.3.5 or, if the TSEC of the sample is 50 mg/g or more, analyze the supernatant from Section 7.3 using gas chromatography. Use a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column under the chromatographic conditions described in Section 7.5. Estimate the concentration factor or dilution factor required to give the optimum concentration for the subsequent GC/MS analysis. In general, the optimum concentration will be one in which the average peak height of the five largest peaks or the height of an unresolved envelope of peaks is the same as that of an internal standard at a concentration of 50-100 µg/ml.

7.3.7 If the optimum concentration determined in Section 7.3.6 is 20 mg of residual material per ml or less, proceed to Section 7.3.8. If the optimum concentration is greater than 20 mg of residual material per ml and if the TSEC is greater than 50 mg/g, apply the GPC cleanup procedure described in Section 7.4. For the GPC cleanup, concentrate 90 ml of the supernatant from Section 7.3.3 or a portion of the supernatant that contains a total of 600 mg of residual material (whichever is the smaller volume). Use the concentration procedure described in Section 7.3.5 and concentrate to a final volume of 15.0 ml. Stop the concentration prior to reaching 15.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume equal to the volume of supernatant used) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out.)

7.3.8 Concentrate further or dilute as necessary an aliquot of the concentrate from Section 7.3.5 or an aliquot of the supernatant from Section 7.3.3, or if GPC cleanup was necessary, an aliquot of the concentrate from Section 7.4.3 to obtain 1.0 ml of a solution having the optimum concentration, as described in Section 7.3.6, for the GC/MS analysis. If the aliquot needs to be diluted, dilute it to a volume of 1.0 ml with methylene chloride. If the aliquot needs to be concentrated, concentrate it to 1.0 ml as decribed in Section 7.3.4. Do not let the volume in the concentrator tube go below 0.6 ml at any time. Stop the concentration prior to reaching 1.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume of 10 ml) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out). Add 250 µl of the internal standard solution, containing 50 µg each of the internal standard, retention time standards, column performance standards, and DFTPP, to 1.0 ml of the final concentrate and save for GC/MS analysis as described in Section 7.5. Calculate the concentration in the original sample that is represented by the internal standard using Equation 3 if an aliquot of the concentrate from Section 7.3.5 was used in Section 7.3.8, Equation 4 if an aliquot of the supernatant from Section 7.3.3 was used in Section 7.3.8 or Equation 5 if an aliquot of the GPC concentrate from Section 7.4.3 was used in Section 7.3.8.

$$\frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.5)}} \times \frac{10}{V_{c\ (7.3.8)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad \text{(Eq. 3)}$$

$$\frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.8)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad \text{(Eq. 4)}$$

$$\frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.7)}} \times \frac{V_F}{V_{GPC\ (7.3.7)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad \text{(Eq. 5)}$$

where:

V_S = Volume of supernatant from Section 7.3.3 used in Sections 7.3.5, 7.3.8, 7.3.7

$V_{C(7.3.8)}$ = Volume of concentrate from Section 7.3.5 used in Section 7.3.8

$V_{F\ (7.3.7)}$ = Final volume of concentrate in Section 7.3.7

V_{GPC} = Volume of GPC concentrate from Section 7.4.3 used in Section 7.3.8

Use this calculated value for the quantification of individual compounds as described in Section 7.7.2.

7.4 Cleanup using gel permeation chromatography

7.4.1 Prepare a 600-mm x 25-mm I.D. gel permeation chromatography (GPC) column by slurry packing using 80 g of Bio-Beads S-X8 that have been swelled in methylene chloride for at least 4 hr. Prior to initial use, rinse the column with methylene chloride at 1 ml/min for 16 hr to remove any traces of contaminants. Calibrate the system by injecting 5 ml of the GPC calibration solution, eluting with methylene chloride at 5 ml/min for 50 min and observing the resultant UV detector trace. The column may be used indefinitely as long as no darkening or pressure increases occur and a column efficiency of at least 500 theoretical plates is achieved. The pressure should not be permitted to exceed 50 psi. Recalibrate the system daily.

7.4.2 Inject a 5-ml aliquot of the concentrate from Section 7.3.7 onto the GPC column and elute with methylene chloride at 5 ml/min for 50 min. Discard the first fraction that elutes up to a retention time represented by the minimum between the corn oil peak and the di-n-octyl phthalate peak in the calibration run. Collect the next fraction eluting up to a retention time represented by the minimum between the coronene peak and the sulfur peak in the calibration run. Apply the above GPC separation to a second 5-ml aliquot of the concentrate from Section 7.3.7 and combine the fractions collected.

7.4.3 Concentrate the combined GPC fractions to 10.0 ml as described in Section 7.3.5. Estimate the TSEC of the concentrate as described in Section 7.3.4. Estimate the TSVC of the concentrate as described in Section 7.3.6.

7.5 Gas chromatography/mass spectrometry

7.5.1 Analyze the 1-ml concentrate from Method 3510, 3540, or 3550, or Section 7.3.8 by GC/MS using the appropriate column (see Section 4.15). The recommended GC operating conditions to be used are as follows:

Conditions for base neutral analysis (3% SP-2250-DB)

Initial column temperature hold: 50° C for 4 min

Column temperature program: 50-300° C at 8 degrees/min

Final column temperature hold: 300^0 C for 20 min.

Conditions for acid analysis (1% SP-1240-DA)

Initial column temperature: 70° C for 2 min

Column temperature program: 70-200° C at 8 degrees/min

Final column temperature hold: 200° C for 20 min

Injector temperature: 300° C

Transfer line temperature: 300° C

Sample volume: 1-2 µl

Carrier gas: Helium at 30 ml/min

7.5.2 If the response for any ion exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

7.5.3 Perform all qualitative and quantitative measurements as described in Sections 7.6 and 7.7. When the extracts are not being used for analyses, store them at 4° C protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

7.6 Qualitative identification. Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

7.6.1 The characteristic ions for each compound of interest must maximize in the same or within one scan of each other.

7.6.2 The retention time must fall within $\pm$ 15 sec (based on the relative retention time) of the retention time of the authentic compound.

7.6.3 The relative peak heights of the characteristic ions in the EICP's must fall within $\pm$20% of the relative intensities of these ions in a reference mass spectrum.

7.7 Quantitative determination

7.7.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used.

7.7.2 Use the internal standard technique for performing the quantification. Calculate the concentration of each individual compound of interest in the sample using Equation 6.

$$\text{Concentration, } \mu g/g = \frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}} \times \frac{A_s}{A_{is}} \times \frac{1}{RF} \qquad \text{(Eq. 6)}$$

where:

$\frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}}$ = internal standard concentration factor calculated in Section 7.3.8

A_s = Area of the primary characteristic ion of the compound being quantified

A_{is} = Area of the primary characteristic ion of the internal standard

RF = Response factor of the compound being quantified (determined in Section 7.1.3).

7.7.3 Report results in μg/g without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

7.7.4 If the surrogate standard recovery falls outside the control limits in Section 8.3, the data for all compounds in that sample must be labeled as suspect.

8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations using a representative sample as a check sample.

8.2.1 Analyze four aliquots of the unspiked check sample according to the method beginning in Section 7.3.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methylene chloride at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples after they have been transferred to centrifuge tubes for extraction. Analyze the spiked aliquots according to the method described beginning in Section 7.3.

8.2.4 Calculate the average percent recovery (R) and the standard deviation of the percent recovery (s) for all compounds and surrogate standards. Background corrections must be made before R and s calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery (s/R x 100) must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.4:

Upper Control Limit (UCL) = R + 3s
Lower Control Limit (LCL) = R - 3s

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the R and s values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standard to monitor spike recoveries. The spiking level used should be that which will give a concentration in the final extract used for GC/MS analysis that is equal to the concentration of the internal standard assuming a 100% recovery of the surrogate standards. For unknown samples, the spiking level is determined by performing the extraction steps in Section 7.3 on a separate aliquot of the sample and calculating the amount of internal standard per gram of sample as described in Section 7.3.8. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as being outside of control limits. The laboratory must monitor the frequency of data so qualified to ensure that it remains at or below 5%. Three surrogate standards, namely decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol, are recommended for general use to monitor recovery of neutral, basic, and acidic compounds, respectively.

8.5 Before processing any samples, the analyst must demonstrate through the analysis of a process blank that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a process blank should be analyzed to determine the level of laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sample technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

8.7 The features that must be monitored for each GC/MS analysis run for quality control purposes and for which performance criteria must be met are as follows:

- Relative ion abundances of the mass spectrometer tuning compound DFTPP.
- Response factors of column performance standards and retention time standards.
- Relative retention time of column performance standards and retention time standards.
- Peak area intensity of the internal standard, e.g., D_{10}-phenanthrene.

8.8 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Tables 1 and 2. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.9 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Tables 1 and 2 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.10 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Tables 4 and 5 were obtained. The standard deviation of the measurement in percent recovery is also included in Tables 4 and 5.

TABLE 4. ACCURACY AND PRECISION FOR BASE/NEUTRAL EXTRACTABLES

Parameter	Reagent water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
Acenaphthene	77	23	83	29
Acenaphthylene	78	22	82	23
Aldrin	72	6	--	--
Anthracene	84	14	76	22
Benzo(a)anthracene	83	19	75	28
Benzo(b)fluoranthene	96	68	41	21
Benzo(k)fluoranthene	96	68	47	27
Benzo(ghi)perylene	80	45	68	40
Benzo(a)pyrene	90	22	43	21
Benzidine	87	61	63	55
Butyl benzyl phthalate	47	32	74	43
β-BHC	69	25	--	--
δ-BHC	56	18	--	--
Bis (2-chloroethoxy) methane	84	33	82	74
Bis (2-chloroethyl) ether	56	36	72	37
Bis (2-chloroisopropyl) ether	71	33	71	39
Bis (2-ethylhexyl) phthalate	129	50	82	63
4-Bromophenyl phenyl ether	80	17	75	20
2-Chloronaphthalene	73	24	79	27
4-Chlorophenyl phenyl ether	45	11	--	--
Chrysene	83	19	75	28
4,4'-DDD	80	9	--	--
4,4'-DDE	69	20	--	--
4,4'-DDT	63	15	--	--
Dibenzo(a,h)anthracene	82	39	70	40
Di-n-butyl phthalate	70	25	93	51
1,2-Dichlorobenzene	59	27	62	28
1,3-Dichlorobenzene	55	28	54	24
1,4-Dichlorobenzene	61	31	63	35
3,3-Dichlorobenzidine	184	174	143	145
Diethylphthalate	42	28	48	28
Dimethyl phthalate	25	33	35	36
2,4-Dinitrotoluene	83	32	79	34
2,6-Dinitrotoluene	79	18	79	25
Di-n-octylphthalate	97	37	89	62
Endosulfan sulfate	79	29	--	--
Fluoranthene	89	19	80	26
Fluorene	77	16	80	20
Heptachlor	69	6	--	--
Heptachlor epoxide	82	7	--	--

TABLE 4. (CONT.)

Parameter	Reagent water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
Hexachlorobenzene	79	20	71	22
Hexachlorobutadiene	46	25	48	28
Hexachlorocyclopentadiene	27	25	12	12
Hexachloroethane	46	21	52	26
Indeno (1,2,3-cd) pyrene	65	37	81	43
Isophorone	75	33	77	42
Naphthalene	67	32	75	35
Nitrobenzene	72	31	82	54
N-Nitrosodi-n-propylamine	68	39	76	45
N-Nitrosodiphenylamine	84	24	86	31
PCB-1221	77	11	--	--
PCB-1254	80	13	--	--
Phenanthrene	84	14	76	22
Pyrene	86	15	80	23
1,2,4-Trichlorobenzene	64	16	69	26

Spiked between 5 and 2400 µg/l.

TABLE 5. ACCURACY AND PRECISION FOR ACID EXTRACTABLES

Parameter	Reagent water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
4-Chloro-3-methylphenol	79	18	75	21
2-Chlorophenol	70	23	71	25
2,4-Dichlorophenol	74	24	80	21
2,4-Dimethylphenol	64	25	58	26
2,4-Dinitrophenol	78	21	108	56
2-Methyl-4,6-dinitrophenol	83	18	90	35
4-Nitrophenol	41	20	43	16
2-Nitrophenol	75	25	75	27
Pentachlorophenol	86	20	66	36
Phenol	36	14	36	21
2,4,6-Trichlorophenol	77	20	81	20

Spikes ranged from 10 to 1500 µg/l.